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The synthesis of a new monomer, N,N-diaminoethyl-4-nitroamiline (DANA), which will be condensed with various diacyl halides to yield polyamides with interesting optical properties was achieved. Several compounds containing potentially 'electrically leaky' atoms between donor (amino) and acceptor (nitro) moieties was prepared. The key finding is that the sulfide is extremely NLO-active.

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Final Technical Report
to
Air Force Office of Scientific Research
Contract No. F49620-85-C-0151
New Non-Linear Optical Polymers

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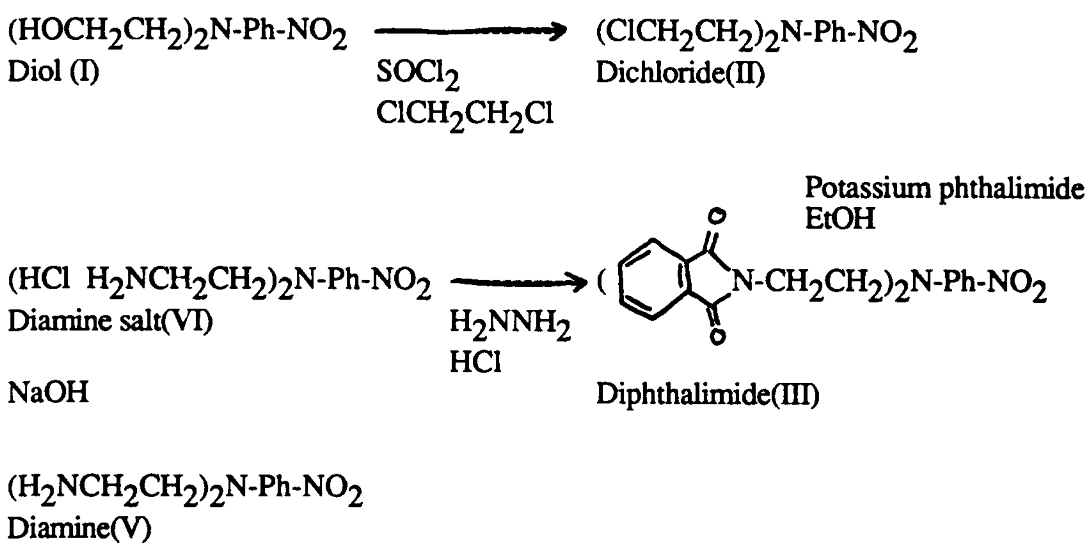
Troy, NY 12180-3590

June, 1988

Summary of Key Results

A. Synthesis of NLO-Active Monomers

We have achieved the synthesis of a new monomer, N,N-diaminoethyl-4-nitroaniline (*DANA*), which will be condensed with various diacyl halides to yield polyamides with interesting optical properties.The total synthesis starting from N,N-dihydroxyethyl-4-nitroaniline (*DHNA*, a monomer also prepared by us for polyester syntheses) is shown below:

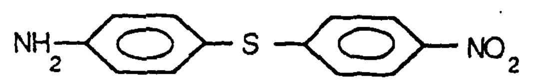
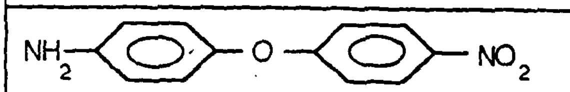
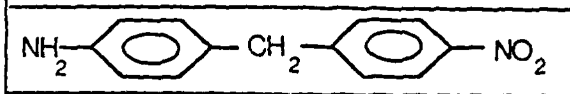
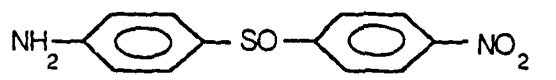
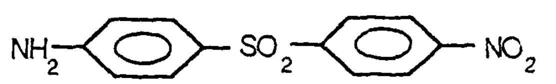


Among the intermediates, diphthalimide(III), diamine salt(VI) and diamine(V) have not been reported in the literature. The compounds have been fully characterized by proton NMR spectroscopy. Details of the sythesis of *DANA* and appropriate intermediates is given in Appendix 1. The systhesis of the corresponding diol, *DHNA*, is reported in Appendix 2. Also reported in Appendix 2 (a Master's Thesis) is the synthesis of new polyesters using *DHNA* as the diol. With our new AFOSR contract, we are investigating the non-linear optical properties of these and related polymers.

B. SHG Activity in Molecules with Various Moieties Separating Donor and Acceptor Groups

We have prepared several compounds containing potentially 'electrically leaky' atoms between donor (amino) and acceptor (nitro) moieties; examples of these "D/A bridges" are shown in the Table below along with melting points of the purified materials.

Table 1

	M. °C
	144-145.5
	133
	98-99
	130-131
	170-171

Our key finding, discussed in more detail in Appendix 3, is that the sulfide is extremely NLO-active. The reason for this is not yet clear. Toward the end of our contract period, we enlisted the aid of a research group at the Jet Propulsion Laboratory with expertise in photophysics of organic molecules. Our aim is to understand the contributions of charge transfer between the aniline and nitrophenyl moieties in the ground and excited states. Our preliminary results suggest that charge transfer is weak in the ground state, but fluorescence is clearly from a charge transfer excited state. A key question is whether this excited state can be populated rapidly enough to contribute to a non-linear optical effect. Very fast kinetic studies are now in progress to address this issue.

Our work under the AFOSR contract has led us to ask extremely fundamental questions about the electronic structure of the molecules shown in Table 1. We are collaborating with theoreticians at S.U.N.Y. Buffalo in an effort to understand what role sulfur plays in any charge transfer interaction, whether it be in the ground and/or excited states. Our recent finding that the methylene bridge is SHG-active (≈ 2x urea) contradicts our earlier observation (Appendix 3; different sample) and begs several important questions. First, a single crystal x-ray study reveals that the methylene bridge is weakly non-centrosymmetric, consistent with the observable SHG. However, our Departmental crystallographer beleives that the compound may exhibit polymorphism, and can in some cases could crytallize centrosymmetrically, accounting for our initial observation of no SHG activity. What is most interesting is that the $-CH_2-$ bridge should be (in our perhaps näive view) an insulator. However, there still may be charge transfer between rings but *through space*, an option well known in chemistry but ignored as far as we are aware as a contributor to SHG. Such charge transfer may for the basis for the design of new classes of non-linear optical organics.

Appendix 1

Appendix 1

SYNTHESIS of *DANA* (V)

1. N,N-dichloroethyl-4-nitroaniline (II)

20.79 g of N,N-dihydroxyethyl-4-nitroaniline(I) were suspended in 300 ml of 1,2-dichloroethane at ambient temperature. The mixture was cooled to 0^oC in an ice-water bath. 18.0 ml of thionyl chloride diluted in 50 ml of 1,2-dichloroethane (precooled to 0^oC) were added in a period of 30 minutes with strong stirring. A yellow solution was obtained upon addition of the thionyl chloride and was refluxed with stirring for 14 hours. The solution was allowed to cool to room temperature and was then diluted with 600 ml of methylene chloride. The solution was stirred in a beaker with 300 ml of dilute aqueous $NaHCO_3$ solution for 30 minutes. Some yellow solid formed during this period was filtered and saved. The organic layer was separated and was extracted with 2 portions of 150 ml water. Upon separation, the solvents were evaporated yielding yellow solid. All of the solid were combined and recrystallized from absolute EtOH twice followed by drying in vacuo at room temperature overnight. 20.77 g of pale yellow crystal were obtained (yield 85.8%).

2. Diphthalimide (III)

16.76 g of N,N-dichloroethyl-4-nitroaniline(II) and 26.32 g of phthalimide potassium derivative were suspended in 110 ml of DMF (analytical reagent grade). The contents were refluxed with stirring for 17 hours and were then cooled to room temperature. Solid product was filtered and recrystallized from gracial acetic acid twice and was dried in vacuo at 60 ^oC overnight. 27.03 g of yellow crystal were obtained (yield 87.6%).

3. N,N-diaminoethyl-4-nitroaniline hydrochloride salt (IV)

26.01 (54 mmol) of diphthalimide(III) were suspended in 420 ml of 95% EtOH and was stirred for 30 minutes. Then, 108 mmol of hydrazine hydrate were added. The contents were heated to reflux. Within about 30 minutes, copious amount of precipitates formed(sometimes, the precipitates were gel-like). The mixture was allowed to reflux for 12 hours and then cooled to room temperature. About 30 ml of concentrated HCl were added to the mixture and the contents were stirred for 30 minutes. The gel-like solid, if any, would become fine powder. The yellowish solid was filtered and was washed with 2 portions of 30 ml of 95% EtOH to white. All filtrates were combined and were allowed to stand at room temperature for 3 hours. During this period, some white precipitates formed and were removed by filtration. Then the filtrate was

evaporated to dry yielding yellow solid. The product was recrystallized from 95% EtOH twice followed by drying in vacuo at room temperature for 24 hours. 13.08 g of product was collected (yield 91.1%).

4. N,N-diaminoethyl-4-nitroaniline(V)

30 ml of 40% NaOH aqueous solution precooled to 0^oC were added to 13.08 g of N,N-diaminoethyl-4-nitroaniline hydrochloride salt (IV) in an ice-water bath. The mixture (orange-colored) was stirred for 30 minutes (sometimes, precipitate formed which was removed by filtration) followed by extraction with at least 6 portions of 200 ml of methylene chloride. Yellow organic layers were combined and dried over Na_2SO_4 for 4 hours. Upon evaporation of the solvent, 7.2 g of crude product were obtained as yellow solid form. Attempts were made to recrystallize the crude product in 95% EtOH but failed. When the product in EtOH was heated to near boiling, orange-colored oil formed which failed to recrystallize even at 0^oC for 24 hours.

Appendix 2

3... - ...

SYNTHESIS AND CHARACTERIZATION OF N,N DIETHANOL-4-NITRO-BENZENAMINE POLY(N,N DIOXYETHYLENE-4-NITRO-BENZENAMINE OXYSEBACOYL), POLY(N,N DIOXYETHYLENE-4-NITRO-BENZENAMINE OXYMALONYL), AND POLY(N,N DIOXYETHYLENE-4-NITRO-BENZENAMINE OXYTEREPHTHALOYL)

Submitted by
Ilya Gorodisher

B.S. Massachusetts Institute of Technology
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

at the
Department of Materials Science and Engineering
Massachusetts Institute of Technology
September, 1986

Signature of Author Ilya Gorodisher
Department of Materials Science and Engineering
August 8, 1986

Certified by Gary E. Wnek
Gary E. Wnek
Thesis Advisor

Accepted by________________________
Bernhardt J. Wuensch
Chairman, Departmental Committee on Graduate Students

SYNTHESIS AND CHARACTERIZATION OF
N,N DIETHANOL-4-NITRO-BENZENAMINE,
POLY(N,N DIOXYETHYLENE-4-NITRO-BENZENAMINE OXYSEBACOYL),
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POLY(N,N DIOXYETHYLENE-4-NITRO-BENZENAMINE OXYTEREPHTHALOYL)

by

Ilya Gorodisher

Submitted to the Department of Materials Science and Engineering on August 8, 1986 in partial fulfillment of the requirements for the Degree of Master of Science in Polymers

ABSTRACT

N,N-diethanol-4-nitro-benzenamine was synthesized via aromatic nucleophilic substitution of 1-chloro-4-nitrobenzene and diethanol amine. This diol was purified and polymerized with sebacoyl chloride, malonyl chloride, and terephthaloyl chloride.

The resulting poly(N,N dioxyethylene-4-nitro-benzenamine oxysebacoyl), poly(N,N dioxyethylene-4-nitro-benzenamine oxymalonyl), and poly(N,N dioxyethylene-4-nitro-benzenamine oxyterephthaloyl) structures were confirmed via NMR, elemental analysis, and IR spectroscopy.

The polymers were characterized via DSC, TGA, X-ray diffraction, and dilute solution viscometry:

Polymer	Crystallinity	Tg (^{o}C)	Approximate Mol. wgt
Sebacoyl	none	below 0	-------n/a--------
Malonyl	none	85.4	-------n/a--------
Terephthaloyl	none	113.2	3,000-8,000

0.25 micron polymer films were poled above their Tg's at 2 MV/cm. Samples are currently being examined for their second harmonic generation (SGH) with Nd+++/YAG laser.

Thesis Supervisor: Dr. Gary E. Wnek

Title: Associate Professor of Polymers

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ACKNOWLEDGEMENTS

U.S. Air Force grant number OSP 97055 is greatly acknowledged. This work would not be possible without my wife's mental and physical support. The author would like to thank Professor G.E. Wnek for his invaluable advice and availablity and Professor D.R. Uhlmann* for his helpful suggestions. The author is deeply indebted to Dr. (in training) Lee Silverman* for numerous discussions, insights, and TGA data.

Great thanks go to Dr. Lin for his time and extensive use of Nd+++/YAG laser.

* Currently at Massachusetts Institute of Technology

INTRODUCTION

Recent advances in technology have created a need for new type of materials. This has been the driving force for the so called "revolution in materials". Perhaps the biggest and the most challenging demand on the mateřials had been placed by the information processing industry.

The computer industry's drive to store as much information as possible in a minimal amount of space and to access it in a shortest time brought forth a new class of materials and processes. New semi-conductive materials, ceramics and polymers were synthesized to meet this challenge.

Very large scale integration (VLSI) requires sharp resolution polymer films for lithography, an art of imprinting VLSI circuits. This type of a photoactive polymer, called a photoresist, needed to be patterned by ultra-violet light and selectively removed on a micron width scale. Now a demand for further intrgration, sub-micron lithography, calls for new polymers that can be patterned by an X-ray source instead of the ultra-violet light. An X-ray source is needed because desired circuits need resolution smaller than the wavelength of

ultra-violet light.

However, the ultimate limit of this technology is not the wavelength of the radiation source. The problem is in the fact that two transmitting wires can lay only so close to each other before the noise level becomes intolerable. This fact turned scientists to look for a new way of transmitting information. Optical information processing looks very promising as a possible replacement for the current technology.

Polymers appear especially attractive as the material for such optical devices. Already, they are employed as optical waveguides, waveguide coatings, in the optical circuits controlling airplane wing surfaces, and graded index lenses. But for optical signal processing via a laser beam, a special class of materials has yet to be developed. These substances have to act as optical switching devices, various modifiers of the laser beam, parity checkers, many other controls for signal processing.

Non-linear optical effects exhibited by some materials greatly simplify the task of making such devices. Optical non-linearity arises due to the non-vanishing x coefficients of non-linear terms in:

$$P = P_o + \chi_1 E + \chi_2 E^2 + \chi_3 E^3 + \ldots +$$

where P is macroscopic polarization and E is the external electric field [32,33].

Currently, there is a lot of interest in the materials with second harmonic generation, or SHG and third harmonic generation, THG. In the first case, χ_2, or quadratic hyperpolarizability, is non-zero. Similarly for TGH, χ_3 must be non-vanishing.

Such materials could be used for frequency doubling or tripling at certain beam intensities. This can be used for night vision, for example, by converting ultra-violet radiation into the visible light.

Three criteria must be met by a material to show second harmonic generation:

1)The molecule must be fairly easily polarizable.

2)Long conjugation lengths are desired.

3)Molecules must be non-centrosymmetric.

The third criterion must be met because when polar molecules crystalize, the oppositely charged ends tend to align. This cancels the net dipole moment of the symmetrical molecules. Non-centrosymmetric molecules have dipole moments that do not line up with the crystal axis. Therefore, there is a net dipole moment that gives rise to quadratic hyperpolarizability [32,33].

The present work deals with synthesis of polymeric materials that may exhibit SGH. The idea was to incorporate nitro-aniline moieties into the backbone of the polymers.

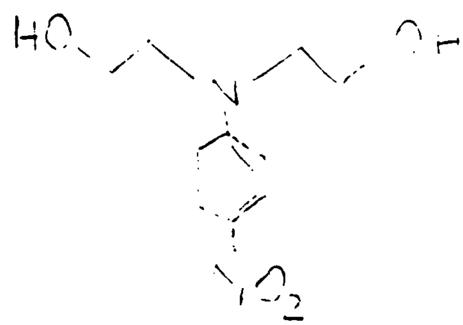
A diol containing the nitro-aniline group was synthesized. Three polyesters were synthesised from a this diol and various diacid chlorides. The structures of the polymers was confirmed by elemental analysis, nuclear magnetic resonance, and infra-red spectroscopy. Polymers were characterized via differencial scanning calorimetry, dilute solution viscometry and X-ray diffraction. Thus, the glass transition temperatures, intrinsic viscosities, and degradation temperatures were found for these polymers.

Polymers of interest were poled above their glass transition temperatures in electric fields of 1-10 MV/cm. A Nd+++/Yag laser was used to determine SGH and quadratic hyperpolirizability of these polymers.

MONOMER PREPARATION

EXPERIMENTAL

The diol 1 was prepared by adding 11.78g (0.075 mole) of



1

1-chloro-4-nitro-benzene to 14.38ml (0.15 mole) of diethanol amine in a 100ml serum-capped round bottom flask. The mixture was stirred in a hot oil bath (110 °C - 116 °C) for 20 hours approximately. The resulting clear orange solution solidified at room temperature into a light orange mixture.

Silica thin layer chromotography was preformed on the mixture in 90% chloroform/10% methanol. The initial spot separated into 3 spots:

TABLE 1

Chemical	Rf
Diethanol amine	0.08
Diol 1	0.40
Chloro-4-nitrobenzene	0.61

These Rf values for 1-chloro-4-nitrobenzene and diethanol amine agreed with those of pure chemicals. The reaction mixture was separated into three components in a silica gel column using 90% chloroform and 10% methanol by volume as the eluting solvent.

The initial separation into three bands of orange, light orange, and yellow, gradually diffused into one continuous yellow band. The eluant (yellow in color) was left overnight in air to evaporate the solvent and bright yellow needle-shaped crystals

resulted. IR (film on NaCl) and NMR (DMSO solvent) spectra are shown in Figures 1 and 2. The melting point (heating at 1.5 degrees C/min.) was 105 °C, at which point the yellow crystal turned into orange liquid and upon cooling changed back to yellow crystal.

TABLE 2

Chemical	Melting point (°C)
Diethanol amine	27-30
Diol	105
Chloro-4-nitrobenzene	83-84
Mixture	41

Elemental analysis (Schwarzkopf Laboratory, Woodside, N.Y.) was as follows:

TABLE 3

Theoretical	Observed

%C	53.08	52.71	
%H	6.25	6.50	
%N	12.38	12.16	
%O	28.29	28.63	(by difference).

Nuclear Magnetic Resonance spectra yielded the following peaks (ppm. vs TMS):

TABLE 4

Chemical shift	peak type	integrated area	assigned # protons	protons assigned
7.6-7.9	doublet	10	2	ortho to nitro-
6.4-6.7	doublet	11	2	meta to nitro-
4.4-4.8	singlet	10.5	2	alcohol
3.4-3.6	singlet	40	8	methylene

Infrared spectra afforded the following absorptions:

TABLE 5

Range (cm^{-1})	Width	Assigned
3600-3150	broad	-OH

3080	sharp	sp2 -C=
2850-2950	broad	sp3 -C-
1915	weak	p-benzene
1725	weak	p-benzene
1580-1600	2-sharp	1,4 di-substituted benzene
1480-1455	2-sharp	aromatic nitro-
1350	sharp	tertiary aromatic amine
1285	weak	tertiary aromatic amine
1060	broad	1,4 di-substituted benzene
1070	weak	1,4 di-substituted benzene
960	broad	aromatic nitro-
850	2-sharp	1,4 di-substituted benzene

The yield of the product was 13 wt.% or 7.6 mol%.

DISCUSSION

Elemental analysis of the product agreed with the theoretical calculation within 0.38% of elemental composition. Integrated NMR peaks yielded the expected distribution of protons. The most deshielded protons are aromatic hydrogens closest to the electron-withdrawing nitro- group. The pair of protons ortho to the electron-donating amine are deshielded less. Methylene and alcohol protons appear in their expected places. Infra-red spectra revealed all the functional groups that were expected and indicated by NMR. Furthermore, the IR of the diol showed a marked absence of the 2 strong and sharp aryl chloride peaks that appeared at 1110 and 1100 cm-1 on the 1-chloro-4-nitrobenzene spectra. The IR spectrum of p-chloro-nitrobenzene can be seen on Figure 1b, and IR spectra of diethanol amine appears on Figure 1c.

Notable shortcomings of this synthesis were the low yield

and tediousness of purification of the diol. Column chromotography allowed only minute amounts of the reaction to be separated. These reasons made it obvious that optimal reaction conditions and different diol extraction proceedure had to be developed for routine bulk synthesis of the diol as a monomer for step polymerization.

In order to fully appreciate the attempts at the bulk separation of the reaction mixture into three pure components one has to understand the principles of thin layer chromotography. A range of solvents of varying polarity was tried on all three components. The results appear in Table 6.

Diethanol amine is the most polar of these substances as the solubility tests indicate. The diol product is a close second; it looses some polarity due to the size of the molecule and due to the benzene ring. However, it is a very bright yellow dye due to the presence of the p-nitro-aniline group, and it tends to color even poor solvents bright yellow. Surprizingly, p-chloro-nitrobezene shows enough non-polar character to easily (20+ g/l) go into carbon tetrachloride.

TABLE 6

SOLVENT	DIETHANOL AMINE	CHLORONITRO BENZENE	N,N DIETHANO[illegible] BENZENA[illegible]
HEXANE	NO	?	NO
CARBON TETRACHLORIDE	NO	YES	NO
TOLUENE	NO	YES	NO
BENZENE	NO	YES	NO
DICHLOROMETHANE	NO	YES	SLIGHT
CHLOROFORM	NO	YES	SLIGHT
ETHYL ETHER	SLIGHT	YES	SLIGHT
ETHYL ACETATE	YES	YES	YES
ACETONE	YES	YES	YES
PROPANOL	YES	YES	YES
ETHANOL	YES	YES	YES
METHANOL	YES	SLIGHT	YES
WATER	YES	NO	SLIGHT

Silica gel chromotography required a mixture of the extreme-most solvents: 90% chloroform and 10% methanol. Less polar p-chloro-nitrobenzene travelled the fastest through the column, not adsorbing to polar silica support. The most polar of the three, diethanol amine adsorbed readily onto the silica, passing through the column the slowest. The desired product (1), eluted between the two substances (see Rf values).

This solvent polarity difference was used to try to separate the reaction mixture via liquid-liquid extraction in water and chloroform and in water and carbon tetrachloride systems. This method did not work because in the first system too much of the product was lost to the chloroform. In general, there was not enough driving force to pull two components into two solutions and leave the pure product as the precipitate. The polarity of the components was too similar to allow for an efficient solvent system choice. Nonetheless, enough diethanol amine was removed to raise the melting point of the mixture to about 60 degrees C.

Another approach for the mixture separation was to use the

basisity difference between the secondary amine in diethanol amine and N,N-diethanol-4-nitro-benzenamine's tertiary amine. Weak acids were used to try to protinate and dissolve diethanol amine while keeping the N,N-diethanol-4-nitro-benzenamine precipitated.

P-chloro-nitrobenzene sublimes readily at room temperature. The idea that did work used the high vapor pressure of the solid p-chloro-nitrobenzene to boil it off at only slightly elevated temperatures. A different reaction mixture separation proceedure was experimentally determined.

BULK MONOMER PURIFICATION

EXPERIMENTAL

P-chloro-nitrobenzene was boiled off under vacuum at 95 ^{o}C for about 1 hour, or about 15 minutes after the visible bubbling of the mixture stopped. At this temperature, p-chloro-nitrobenzene and diethanol amine coexist as two immiscible liquids, with p-chloro-nitrobenzene occupying the lower level. When p-chloro-nitrobenzene boils, it has to go through the layer of diethanol amine, bringing forth extensive bubbling. See Figure 3 for the details of the apparatus.

An equal volumetric amount of cold water was added to the remainder of the mixture, which was stirred for 15 minutes and suction filtered. This was repeated two or three times, depending on the consistency of the mixture and appearence of the precipitate (bright yellow color is optimal).

The precipitate was recrystallized in water to remove traces of diethanol amine and p-chloro-nitrobenzene. The latter does not dissolve in boiling water to appreciable amount, but

N,N-diethanol-4-nitro-benzenamine readily goes into hot water in large amounts. So the mixture was suction filtered hot to remove any residual p-nitro-chlorobenzene.

The precipitate from the cooled water was recrystallized from chloroform to remove any diethanol impurity that might have co-precipitated with N,N-diethanol-4-nitro-benzenamine. Here residual water from the previous step formed an immiscible layer with the chloroform. All of diethanol amine readily went into the aqueous layer, which was subsequently removed.

The precipitate from the chloroform recrystallization was dryed over P_2O_5 in vacuum to remove any water that was dissolved in hot chloroform. Clearly, residual diethanol amine would prefer to go into the aqueous layer over the solution of chloroform and miniscule amount of water. Melting point of the dry product was $105^{o}C$.

DISCUSSION

Advantages of this separation method are obvious. Any volume of the reaction mixture can be routinely separated, this is especially useful for the semi-industrial amounts of the monomer

that are needed for polymerizations.

The speed of this method greatly exceeds that of the column chromotography. Roughly five hours are needed here to purify several grams of N,N-diethanol-4-nitro-benzenamine, whereas column separation took well over two days. Furthermore, five hours can be cut down to three, if equipment is available to boil off residual water at temperatures below 120 ^{o}C instead of drying over phosphorus pentoxide.

Most of this time, there is no need for the presense of the researcher in the lab, whrereas column chromotography required continuous feeding of solvent at exact times. So, the tediousness of the process has been greatly alleviated.

The yield of the reaction was increased by 52% to 11.6 molar percent or 16.7 wt%.

A range of reaction times and temperatures was tried. It was determined that at temperatures higher than ca. 125 ^{o}C there is a side reaction that degrades the desired product to form bright orange crystals with a melting point around 175 ^{o}C. These crystals are insoluble in the solvents listed in Table 6. Analysis of TLC as above indicated that orange crystals are

aromatic, anilinic and non-polar, travelling almost with the solvent front ahead of p-chloro-nitrobenzene.

The reaction extent at 125 ^{o}C for 69 hours was nearly 80% based on the amounts of p-chloro-nitrobenzene left. However, most of the product was degraded. Optimal reaction conditions were found to be 20 hours at 115-120 ^{o}C with the yields of 11.6 molar percent.

The orange byproduct was dissolved in dioxane and its chemical composition was determined by NMR and IR spectroscopy. (See Figure 4 and 5)

TABLE 7

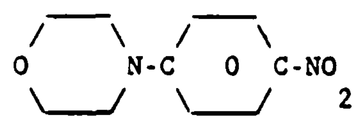
Chemical shift	peak type	integrated area	assigned # protons	protons assigned
7.95,7.8	doublet	9	2	ortho to nitro-
6.4-6.7	doublet	8	2	meta to nitro-
3.3-3.7	singlet	36	8	methylene

Infrared spectra afforded the following absorptions:

TABLE 8

Range (cm^{-1})	Width	Assigned
3100	broad	sp2 -C=
2970	sharp	sp3 -C=
1590,1570	2-sharp	para-benzene
1477	sharp	nitro-
1400	sharp	nitro-, para-benzene
1380	weak	tertiary aromatic amine
1300,1260	2-sharp	tertiary aromatic amine
1210,1145	2-sharp	tertiary aliphatic amine
1100	sharp	aliphatic ether
1080,1000	2-sharp	para-benzene
945	sharp	nitro-
800	sharp	para-benzene

The spectra seem to indicate that the orange crystals are 1-nitro-4-benzoxazine ($C_{10}H_{12}N_2O_3$):



The NMR spectrum shows that the benzene protons meta- to the nitro- group have deshielded farther, closer to the ortho- peaks. Apparently the solvent. trifluoroacetic acid, protonates the

tertiary amine and tends to withdraw the electrons from the amine group, thus making it also electron withdrawing from the benzene.

IR spectra shows the presence of a cyclic ether as indicated by a sharp peak at 1100 cm-1. Even more clearly seen on this spectra is the absence of the broad hydroxide stretch at 3500-3100 cm-1.

Cyclic ether formation from a diol condensation at higher temperatures and under acidic conditions is well documented in the literature [8-12]. In the given reaction, one -OH group becomes protinated by HCl's cation and leaves as water. Oxygen from the other -OH group attacks the carbon cation and thus closes the ether ring. H+ leaves the ring and restores the charge balance. HCl here is a byproduct of the nucleophilic aromatic substitutions. The yield of the 1-nitro-4-benzoxazine varied from 0 to 20% depending on temperature. It was easy to remove from the reaction mixture due to its solubility. Therefore, the yield of the diol could be further increased by running the reaction for shorter times and higher temperatures (10 hours, 125 ^{o}C) and washing out the orange crystals with acetone.

POLYMER PREPARATION

SEBACOYL

EXPERIMENTAL

A polyester was prepared from sebacoyl chloride and N,N-diethanol-4-nitro-benzenamine via solution and melt polymerizations.

1.060 grams of N,N-diethanol-4-nitro-benzenamine (0.00469 mole) were added to 1 ml of sebacoyl chloride (0.00469 mole) in a nitrogen purged round bottom flask. The reaction mixture was stirred at room temperature for five minutes and then was placed in hot oil at 155 ^{o}C. The reaction temperature was then ramped to 250 ^{o}C. Throughout the reaction, the HCl gaseous product was allowed to escape. At 190 ^{o}C, the mixture began to darken and eventually turned black. At temperatures above 180 ^{o}C the mixture was a viscous fluid

The polymer was then separated from the degraded product in

acetone/ silica gel column. Acetone soluble polymer turned out to be a sticky oily substance, apparently of low molecular weight.

The reaction was then run in dioxane that had been dried with sodium benzophenone. The same amounts of the reactants were transfered into evacuated Schlenk tube, containing dry dioxane (100 ml) and 1.305 ml of triethyl amine (0.00938 mole) dried over NaOH pellets.

Triethyl amine hydrochloride precipitated out of solution and was removed via suction filtration. Dioxane was dried at room temperature to separate the polymer.

The polymer was then analyzed via NMR, IR, and elemental analysis:

Elemental analysis (Schwarzkopf Laboratory, Woodside, N.Y.) was as follows:

TABLE 9

Observed	Theoretical

%C	58.91	61.2
%H	7.62	7.2
%N	7.20	7.2
%O	26.27	24.5 (by difference).

Nuclear Magnetic Resonance spectra yielded the following peaks (ppm. *vs* TMS) (See Figure 6)

TABLE 10

Chemical shift	peak type	integrated area	#	assigned protons / protons assigned
8.33,8.18	doublet	12	2	ortho to nitro-
6.96,6.77	doublet	12	2	meta to nitro-
4.32,4.23	doublet	24	4	O(CH2)-----(CH2)O
3.75	doublet	25	4	CH2-N-CH2
2.3,2.2	doublet	25	4	O=C(CH2)---(CH2)C=O
1.51	singlet		4	O=C-CH2-CH2-(CH2)4-CH2-CH2-C=O
1.40	singlet	73-74	4	O=C-(CH2)2-CH2-(CH2)2-CH2-(CH2)2-C=O
1.27	singlet		4	O=C-(CH2)3-(CH2)2-(CH2)3-C=O

Infrared spectra afforded the following absorptions (See Figure 7):

TABLE 11

Range (cm^{-1})	Width	Assigned
2950,2875	2-sharp	sp3 -C-
1745	sharp	ester
1600	sharp	1,4 di-substituted benzene
1500,1520	2-sharp	aromatic nitro-p-benzene
1400	medium	aromatic nitro-
1325	sharp	tertiary aromatic amine
1210	sharp	ester
1175	broad	ester
1115	sharp	1,4 di-substituted benzene
835	medium	1,4 di-substituted benzene
760	medium	methylene

DISCUSSION

The polymer was confirmed to be poly-(N,N dioxyethylene-4-nitro-benzenamine-oxysebacoyl), PDNBAS. At room temperature it was a sticky, viscous solid. Freezing in liquid nitrogen embrittled the product, proving that the polymer was above Tg at room temperature.

Elemental analysis results differed from the calculated by 0.42% (5.5% error) for hydrogen, by 2.29% (3.9% error) for carbon, by 1.77% (6.7% error) for oxygen. The nitrogen results were exact. Although the error between the theoretical and observed data is slightly greater than normal, it can be explained by two arguments. A polymer probably retained water during the removal of salt in water. This is indicated by the higher oxygen and hydrogen content and lower carbon content.

Another reason for the error is the chain end effects in the low molecular weight polymer. This fact was indicated by the brittleness of the polymer.

NMR results excellently agree with expected spectra for poly-(N,N dioxyethylene-4-nitro-benzenamine-oxysecacoyl). Four aromatic protons are split into doublets as in the monomeric diol. This is due to the electron donating effect of the amine and electron withdrawing effect of the nitro- group deshield four benzene protons in symmetric ortho- and para- pairs.

Polymer's newly formed ester deshields neighbouring methylene protons stronger than monomer's alcohol. This destroys the monomer's symmetrical deshielding between -OH adjacent methylenes and amine adjacent methylenes. For this reason, -OH adjacent methylenes peak 4.32 ppm and 4.23 ppm vs TMS, a bit farther amine adjacent methylenes. The rest of aliphatic protons show the symmetry between sebacoyl methylenes.

The IR spectrum further confirms ester formation.

MALONYL

EXPERIMENTAL

1 ml of malonyl chloride (0.0103 mole) was added to 2.323 grams of N,N-diethanol-4-nitro-benzenamine (0.0103 mole) and 2.86 ml of triethyl amine (0.0206 mole) in an evacuated Schlenk tube, containing dry dioxane. Polymerization was carried out in two different ways: in boiling dioxane and in dioxane at room temperature. All the reported results are for the boiling solution polymerization. The polymer precipitated out of solution with triethyl amine hydrochloride. Some oligomeric matter stayed in dioxane. The polymer was washed twice with water to remove all the salt. Elemental analysis (Schwarzkopf Laboratory, Woodside, N.Y.) was as follows:

TABLE 12

	Observed	Theoretical	
%C	52.35	53.06	
%H	5.04	4.76	
%N	8.77	9.52	
%O	33.84	32.64	(by difference).

Nuclear Magnetic Resonance spectra yielded the following peaks (ppm. vs TMS), (See Figure 8):

TABLE 13

Chemical shift	peak type	integrated area	assigned # protons	protons assigned
8.08,7.81	doublet	11	2	ortho to nitro-
6.97,6.80	doublet	11	2	meta to nitro-
4.35,4.23	broad	12	2	malonyl methylenes
3.75	broad	44	8	-CH2-CH2-N-CH2-CH2-

Infrared spectra afforded the following absorptions, (See Figure 9):

TABLE 14

Range (cm^{-1})	Width	Assigned
3650-3200	broad	H2O's -OH stretch
3100	weak	sp2 -CH=
2950	broad	sp3 -CH-
2690	weak	triethyl amine hydrochloride
2500	weak	triethyl amine hydrochloride
1750	broad	ester
1600	sharp	1,4 di-substituted benzene
1515,1490	2-sharp	aromatic nitro-p-benzene
1400	medium	aromatic nitro-
1310	broad	tertiary aromatic amine
1200	sharp	ester
1175	broad	ester
1110	sharp	1,4 di-substituted benzene
835	medium	1,4 di-substituted benzene
760	medium	methylene

Differential scanning calorimetry showed a glass transition temperature in the 72-100 ^{o}C range and 85 ^{o}C midpoint (See Figure

10). Also, there was a pronounced lack of crystallinity indicated by absence of the melting point. This fact was confirmed by X-ray diffraction; the spectra had no peaks, even at the highest sensitivity settings (See Figure 11). Thermal Graviometric Analysis indicated a degradation temperature of approximately 250 ^{o}C (See Figure 12).

DISCUSSION

The synthesised polymer was confirmed to be poly-(N,N dioxyethylene-4-nitro-benzenamine-oxymalonyl), PDNBAM. At room temperature the polymer was a bright yellow powder. The melt cast film was brittle, indicating a low molecular weight. The polymer was insoluble in common solvents listed in Table 6. An oligomeric fraction was collected from dioxane and was found to be acetone soluble.

The polymerization in boiling dioxane was carried out because the polymer precipitated out of the solution at room temperature before significant molecular weight was achieved. The polymer solubility in boiling dioxane was quite a bit higher (16g/l).

Elemental analysis results differed from the calculated by 0.28% (5.6% error) for hydrogen, by 0.71% (1.3% error) for carbon, by 1.2% (3.5% error) for oxygen, and 0.75% (8.6% error) for nitrogen. These results agreed quite a bit better than the sebacoyl case. This was due to the higher molecular weight

of this polymer. Analysis of the chain end effect in low molecular weight polymers/oligomers of PDNBAM on the elemental analysis appears in Tables 15-20. Also in those Tables are computations of elemental compositions of polymers containing

TABLE 15: 5% WATER/PONBAM RU
EFFECT OF WATER ON PONBAM ELEMENTAL ANALYSIS

RU	%C	%H	%N	%O
THEORY	53.1	4.8	9.5	32.6
OBSEREVED	52.35	5.04	8.77	33.84
5	52.261306533	4.8576214405	9.3802345059	33.500837521
7	52.442011238	4.8359986553	9.4126686837	33.309321423
9	52.542943752	4.8239212604	9.430784778	33.202350211
11	52.607376069	4.8162114105	9.4423495509	33.134062969
13	52.652075707	4.8108627359	9.4503725628	33.086688994
15	52.684903749	4.8069345942	9.4562647754	33.051896882
17	52.71003518	4.8039274144	9.4607755451	33.025261861
19	52.729892726	4.8015512978	9.46433972	33.004216257
21	52.745978844	4.7996264632	9.4672269719	32.987167721
23	52.759274781	4.7980354963	9.4696134221	32.973076301
25	52.770448549	4.7966984642	9.4716189703	32.961234017
27	52.779970678	4.7955590642	9.4733280704	32.951142188

TABLE 16: 10% WATER/PONBAM RU

RU	%C	%H	%N	%O
THEORY	53.1	4.8	9.5	32.6
OBSEREVED	52.35	5.04	8.77	33.84
5	52.104208417	4.8764195057	9.3520374081	33.667334669
7	52.283826487	4.8549267452	9.3842765489	33.476970219
9	52.384150437	4.84202217	9.4022834117	33.370643987
11	52.448193655	4.8352588789	9.4137783483	33.302769118
13	52.492623078	4.8299425377	9.4217528[illegible]92	33.255681524
15	52.525252525	4.8260381594	9.4276094276	33.221099888
17	52.550231839	4.8230491816	9.4320928942	33.194626085
19	52.569969139	4.8206874534	9.4356354865	33.173707921
21	52.585957816	4.8187742785	9.438505249	33.156762657
23	52.59917319	4.8171929516	9.4408772393	33.142756819
25	52.610279239	4.8158640227	9.4428706327	33.130986105
27	52.619743647	4.8147315294	9.4445693726	33.120955451

TABLE 17: 15% WATER/PONBAM RU

RU	%C	%H	%N	%O
THEORY	53.1	4.8	9.5	
OBSEREVED	52.35	5.04	8.77	
5	51.948051948	4.8951048951	9.324009324	33.83
7	52.126593155	4.87374099	9.3560551816	33.64
9	52.226314027	4.8618085779	9.3739537998	33.53
11	52.289971661	4.8541914252	9.3853795289	33.47
13	52.334133313	4.848907125	9.3933059792	33.42
15	52.366565962	4.8450262952	9.3991272239	33.38
17	52.391394536	4.8420553547	9.4035836346	33.36
19	52.411012678	4.8397078846	9.4071048397	33.34
21	52.426904796	4.8378062637	9.4099572711	33.32
23	52.440040338	4.8362344894	9.4123149325	33.31
25	52.451079282	4.8349135902	9.4142962814	33.29
27	52.460486493	4.8337879411	9.4159847551	33.28

TABLE 18: 20% WATER/PONBAM RU

RU	%C	%H	%N	%O
THEORY	53.1	4.8	9.5	
OBSEREVED	52.35	5.04	8.77	
5	51.792828685	4.9136786189	9.2961487384	33.997
7	51.970302684	4.8924424139	9.3280030459	33.809
9	52.069425901	4.8805815161	9.3457943925	33.70
11	52.132701422	4.8730100863	9.3571515372	33.637
13	52.176597715	4.8677575383	9.3650303592	33.590
15	52.208835341	4.8639000446	9.3708165997	33.556
17	52.233514536	4.8609469786	9.3752461987	33.530
19	52.253014597	4.858613638	9.3787462097	33.509
21	52.268811028	4.8567234667	9.3815814666	33.492
23	52.281867459	4.8551611587	9.3839249286	33.473
25	52.292839903	4.8538482167	9.3858943416	33.467
27	52.302190434	4.8527293498	9.3875726419	33.457

TABLE 19: 25% WATER/PDNBAM RU

RU	%C	%H	%N	%O
THEORY	53.1	4.8	9.5	32.6
OBSEREVED	52.35	5.04	8.77	33.84
5	51.638530288	4.9321416749	9.2684541543	34.160873883
7	51.814946619	4.9110320285	9.300118624	33.973902728
9	51.913477537	4.8992420041	9.3178036606	33.869476798
11	51.976374375	4.8917158867	9.3290928366	33.802816901
13	52.020007695	4.8864948057	9.3369244581	33.756573041
15	52.052052052	4.8826604382	9.3426760093	33.7226115
17	52.076583211	4.8797250859	9.3470790378	33.696612666
19	52.095966254	4.8774057474	9.3505580455	33.676069953
21	52.11166786	4.8755269228	9.3533762825	33.659428935
23	52.124645892	4.8739739958	9.355705673	33.645674439
25	52.135552436	4.8726689392	9.3576632578	33.634115367
27	52.144846797	4.8715567936	9.3593314763	33.624264933

TABLE 20: 40% WATER/PDNBAM RU

RU	%C	%H	%N	%O
THEORY	53.1	4.8	9.5	32.6
OBSEREVED	52.35	5.04	8.77	33.84
5	51.181102362	4.9868766404	9.186351706	34.645663291
7	51.354401806	4.9661399549	9.2174567344	34.462001505
9	51.451187335	4.9545587804	9.234828496	34.359425388
11	51.5129683	4.9471661864	9.2459173871	34.293948127
13	51.555826724	4.9420378279	9.2536099248	34.248525524
15	51.587301587	4.9382716049	9.2592592593	34.215167549
17	51.611396544	4.9353884478	9.263583995	34.189631014
19	51.630434783	4.9331103679	9.2670011148	34.169453735
21	51.645856981	4.9312649767	9.2697692017	34.153108841
23	51.658604008	4.9297396913	9.2720571297	34.139599171
25	51.669316375	4.9284578696	9.2739798622	34.128245893
27	51.67844523	4.9273655281	9.2756183746	34.118570868

various amounts of H_2O. This was done because here, as in the case of PDNBAS, the salt was removed with water. The retained water incresed the amount of oxygen and hydrogen, and decreased the the carbon content.

NMR conclusively proves the structure for this polymer. The dioxane peak at 3.58 ppm vs TMS interfered with integration of the aliphatic peak of eight methylene protons at 3.77 ppm vs TMS. However, dioxane peak area can be easily subtracted from the aliphatic peak, as the break in the integral indicates.

Unfortunately, the polymer sample for the IR spectrum was not washed well enough with water, and some triethyl amine hydrochloride is still visible in the spectrum as well as water. Nonetheless, IR analysis showed an ester carbonyl stretch indicating formation of a polyester.

A good polymerization solvent is yet to be found for this polymer. The product of the boiling dioxane polymerization did not dissolve in any of attempted solvents.

TEREPHTHALOYL

EXPERIMENTAL

A. Solution Polymerization

1.7953 grams of terephthaloyl chloride (0.00884 mole) was added to 2.000 grams of N,N-diethanol-4-nitro-benzenamine (0.00884 mole) and 2.46 ml of triethyl amine (0.01768 mole) in an evacuated Schlenk tube, containing dry dioxane. Polymerization proceeded at room temperature.

B. Bulk Polymerization

Equimolar quantities of the diol and the diacid chloride were allowed to react in a round bottom flask under nitrogen at 135 ^{o}C for 2 hours. HCl was allowed to escape with the nitrogen. It was observed that at that temperature no liquid was formed, even though the melting point of diol was 105 ^{o}C and melting point of

diacid was 78 ^{o}C. Apparently in this case low molecular weight was a result of diffusion controlled reaction. Yet the temperature of the reaction can not be raised due to the reasons discussed in the monomer section. This polymer was not used in the analysis. All the tests were performed on the solution polymerized product.

Triethyl amine hydrochloride and the polymer precipitated out of solution and were removed via suction filtration. The polymer was washed twice in cold water and dried at 100 ^{o}C to remove the salt and water.

The polymer was then analyzed via NMR, IR, and elemental analysis:

Elemental analysis (Schwarzkopf Laboratory, Woodside, N.Y.) was as follows:

TABLE 21

	Observed	Theoretical
%C	59.37	60.7

%H	4.50	4.6	
%N	7.34	7.9	
%O	28.79	26.8	(by difference).

Nuclear Magnetic Resonance spectra yielded the following peaks (ppm. _vs_ TMS) (See Figure 13):

TABLE 22

Chemical shift	peak type	integrated area	# assigned protons	protons assigned
8.25	doublet		2	ortho- to nitro-
8.10	doublet	91-92	2	meta- to nitro-
7.95	singlet		4	terephthaloyl
4.73,4.47	singlet	93-95	8	methylene

Infrared spectra afforded the following absorptions (See Figure 14):

TABLE 23

Range (cm^{-1})	Width	Assigned
3100	weak	sp2 -CH=
2980,2910	weak	sp3 -CH-

1800	sharp	aromatic
1730	broad	ester
1600	broad	1,4 di-substituted benzene
1500,1520	2-sharp	aromatic nitro-p-benzene
1460,1440	2-sharp	aromatic nitro-p-benzene
1415,1395	2-sharp	conjugated ester
1320,1270	sharp	tertiary aromatic amine
1210	sharp	ester
1110	broad	p-benzene
1000,1020,1040	sharp	p-benzene
915	weak	ethyl alcohol
880,830	sharp	p-benzene
755,730	2-sharp	methylene

Differential scanning calorimetry showed a glass transition temperature in the 116-133 ^{o}C range and 123 ^{o}C midpoint (See Figure 15). Also, there was a pronounced lack of crystallinity indicated by absence of the melting point. This fact was confirmed by X-ray diffraction; the spectrum had no peaks, even at the highest sensitivity settings (See Figure 16). DSC indicated that the

polymer began degrading at approximately 210 C.

The polymer was found to be soluble in m-chlorophenol and trifluoroacetic acid. Dilute solution viscometry was performed for various polymer concentrations in three solvent systems:

1) trifluoroacetic acid (See Figure 17)

2) m-chlorophenol (See Figure 18)

3) Equal volumetric mixture of the two (See Figure 19)

using a Fenske viscometer. Run times and calculated viscosities appear in Table 24. Intrinsic viscosities were determined by extrapolating to zero concentration for each system. An attempt was made to relate these to average molecular weight of the polymer using Mark-Houwink constants for poly-(ethylene terephthalate) [13-18]. Molecular weight was approximated to be in the 5000 +/- 2000 range by averaging all molecular weights from Table 31 and adding/subtracting the standard deviation.

Polymer concentrations were confirmed immidiately following the viscometry runs by evaporating a known volume of solution and weighing the amount of polymer.

TABLE 24: PDNBAT VISCOSITIES AND RUN TIMES

CONC g/ml	FL TIME seconds	NR	NSP	NSP/C	LN(NR)/C
------------TEREPHTHALOYL VISCOSITY IN m-CHLOROPHENOL------------					
0	844				
0.0041	955	1.1315	0.1315	32.077	30.13630
0.00656	1021	1.2097	0.2097	31.968	29.02215
0.01053	1185	1.4040	0.4040	38.369	32.22654
--------------TEREPHTHALOYL VISCOSITY IN TRIFLUOROACETIC ACID---					
0	40	0.0008			
0.00414	42.5	1.0705	0.0705	17.051	16.47612
0.01054	45.8	1.1623	0.1623	15.406	14.27635
----------TEREPHTHALOYL VISCOSITY IN 50/50 TFA AND M-CHLOROPHENO					
0	199				
0.00527	211.25	1.0615	0.0615	11.680	11.33537
0.01541	265.25	1.3329	0.3329	21.603	18.64814
0.01656	272	1.3668	0.3668	22.151	18.87060
0.01757	259	1.3015	0.3015	17.160	14.99847
0.0207	280	1.4070	0.4070	19.663	16.49684

DISCUSSION

A bright yellow polymer was confirmed to be poly-(N,N dioxyethylene-4-nitro-benzenamine-oxyterephthaloyl), PDNBAT. A thin freestanding film was melt cast from it. The film was brittle at room temperature, suggesting a low molecular weight (in the thousands).

Elemental analysis results differed from the calculated by 0.1% (2.2% error) for hydrogen, by 1.33% (2.2% error) for carbon, by 1.99% (6.9% error) for oxygen, and 0.56% (7.6% error) for nitrogen. The results for oxygen and carbon agreed quite a bit better than the sebacoyl case. However, the nitrogen error was higher, indicating chain end and retained water effect for the low molecular weight (see PDNBAS and PDNBAM discussions). The study of chain end and retained water effect on PDNBAT and on the oligomers appear on Tables 25-30.

NMR confirms the structure of the polymer. Theoretically, one would expect all of the terephthaloyl protons to be deshielded to the same extent (i.e. they are equivalent) since

they are completely symmetrical. In the spectrum this singlet appears at 7.95 ppm vs TMS. Unfortunately, this peak obscures the second doublet of the nitro-aniline, but integration confirms

TABLE 25: 5% H_2O PER REPEAT UNIT OF PDNBAT
EFFECT OF WATER CONTENT ON PDNBAT ELEMENTAL ANALYSIS
0.05

RU	%C	%H	%N	%O
THEORY	60.67	4.53	7.86	26.94
OBSEREVED	59.37	4.6	7.34	28.69
5	59.916782247	4.5769764216	7.7669902913	27.73925104
7	60.088224774	4.5582800143	7.7892143226	27.564290889
9	60.183895235	4.5478468159	7.801616049	27.4666419
11	60.244935216	4.5411901924	7.8095286392	27.404345952
13	60.287266247	4.5365738455	7.815015995	27.361143912
15	60.31834683	4.5331843991	7.8190449595	27.329423811
17	60.342135967	4.5305901106	7.8221287365	27.305145198
19	60.360930123	4.5285405421	7.824565018	27.285964319
21	60.376153017	4.5268804323	7.826538354	27.270428197
23	60.388734243	4.5255084056	7.8281692538	27.257588097
25	60.399306526	4.5243554611	7.8295397349	27.248798278
27	60.408315466	4.5233730048	7.8307075604	27.237683969

TABLE 26: 10% WATER/PDNBAT RU
0.1

RU	%C	%H	%N	%O
THEORY	60.67	4.53	7.86	26.94
OBSEREVED	59.37	4.6	7.34	28.69
5	59.767570559	4.5932484781	7.7476480354	27.891532928
7	59.938159042	4.5746452073	7.7697813573	27.717434393
9	60.033351862	4.5642640973	7.7821011673	27.620282873
11	60.094086701	4.5576407507	7.789974202	27.558298346
13	60.136205937	4.5530475007	7.7954341029	27.51531246
15	60.167130919	4.5496750232	7.7994428969	27.483751161
17	60.190800905	4.5470937205	7.8025112284	27.459594138
19	60.209500895	4.5450544292	7.8049353012	27.440509375
21	60.224647495	4.5434026395	7.8068987493	27.425051117
23	60.237165652	4.5420374906	7.8085214734	27.412275334
25	60.247684927	4.5408903269	7.8098850831	27.401539663
27	60.256640659	4.5399127973	7.8110470525	27.392391462

TABLE 27: 15% WATER/PONBAT RU

0.15

RU		%C	%H	%N	%O
THEORY		60.67	4.53	7.86	26.94
OBSEREVED		59.37	4.6	7.34	28.69
	5	59.619100193	4.6094396909	7.7284018769	28.043058239
	7	59.788840998	4.5909288624	7.7504053146	27.869824825
	9	59.883558745	4.5805994517	7.7626836706	27.773157133
	11	59.943991725	4.5740091329	7.7705174458	27.711481696
	13	59.98590075	4.5694388071	7.7759500972	27.668710346
	15	60.016671298	4.5660831713	7.7799388719	27.637306659
	17	60.040223025	4.563514773	7.7829918736	27.613270328
	19	60.058829555	4.5614856658	7.7854038312	27.594280948
	21	60.073900433	4.5598421338	7.7873574635	27.57889937
	23	60.086355995	4.5584838113	7.7889720734	27.566188121
	25	60.096822659	4.557342385	7.7903288632	27.555506093
	27	60.105741582	4.5563697451	7.7914850199	27.546403653

TABLE 28: 20% WATER/PONBAT RU

0.2

RU		%C	%H	%N	%O
THEORY		60.67	4.53	7.86	26.94
OBSEREVED		59.37	4.6	7.34	28.69
	5	59.471365633	4.6255506608	7.7092511013	28.193832599
	7	59.640265068	4.6071315873	7.7311454718	28.021457873
	9	59.734513274	4.5968534907	7.7433628319	27.925270403
	11	59.794644655	4.5902959533	7.7511576404	27.863901752
	13	59.836345039	4.5857483805	7.7565632458	27.821343334
	15	59.866962306	4.5824094605	7.7605321508	27.790096083
	17	59.89039666	4.5798538622	7.7635699374	27.766179541
	19	59.908910429	4.577834871	7.7659698704	27.74723483
	21	59.923906151	4.576199535	7.7679137603	27.731980554
	23	59.936299585	4.5748479876	7.7695203166	27.719332111
	25	59.946714032	4.5737122558	7.7708703375	27.708703375
	27	59.955588453	4.5727444691	7.7720207254	27.699646352

TABLE 29: 25% WATER/PDNBAT RU

0.25

RU	%C	%H	%N	%O
THEORY	60.67	4.53	7.86	26.94
OBSEREVED	59.37	4.6	7.34	28.69
5	59.324361439	4.641581983	7.6901950014	28.343861576
7	59.492425733	4.6232539839	7.7119811135	28.17233917
9	59.586206897	4.6130268199	7.724137931	28.076628352
11	59.646039915	4.60650182	7.731894063	28.015564202
13	59.687533213	4.6019768307	7.7372728239	27.973217133
15	59.717998341	4.5986545019	7.7412220072	27.94212515
17	59.741316196	4.5961116082	7.7442446921	27.918327503
19	59.759737896	4.5941026574	7.7466326902	27.899526756
21	59.774659024	4.5924754563	7.7485669105	27.88429861
23	59.786990794	4.5911306336	7.7501654733	27.871713099
25	59.797353413	4.5900005537	7.7515087758	27.861137257
27	59.806183664	4.589037584	7.7526534379	27.852125314

TABLE 30: 40% WATER/PDNBAT RU

0.4

RU	%C	%H	%N	%O
THEORY	60.67	4.53	7.86	26.94
OBSEREVED	59.37	4.6	7.34	28.69
5	58.887677208	4.6892039258	7.6335877863	28.78953108
7	59.053272926	4.6711451336	7.6550538978	28.620528042
9	59.145673604	4.6610685165	7.6670317634	28.526226117
11	59.204624738	4.654639689	7.6746735772	28.466061995
13	59.24550595	4.6501814499	7.6799729935	28.424339607
15	59.275521405	4.6469081595	7.6838638858	28.39370655
17	59.298494929	4.6444028184	7.6868419353	28.370260319
19	59.316644505	4.6424235417	7.689194658	28.351737295
21	59.331345158	4.640820384	7.6911002982	28.33673416
23	59.343494672	4.639495437	7.6926752353	28.324334655
25	59.353704111	4.638382062	7.693998681	28.313915146
27	59.362403811	4.6374333293	7.6951264199	28.30503644

that it is there. Aliphatic and aromatic areas are roughly equal, as expected.

Here, like in the case of the p-nitro-benzoxazine, the protons meta- to the nitro- group deshielded closer to the ortho-protons and farther <u>vs</u> TMS. This indicates that the amine group is no longer donating, but rather electron withdrawing. This effect is due to the protonation of the tertiary amine by trifluoroacetic acid, which was the solvent in both systems. Protonated amine is electron withdrawing due to its positive charge.

Once again, IR spectra support the formation of polyester.

M-chlorophenol has a melting range of 33-35 ^{o}C. The 98% purity chemical recieved from Aldrich was a liquid at room temperature. Therefore, it must have contained significant amounts of impurities. The density of the substance was measured to be 1.235g/ml, which is a bit lower than the reported value of 1.268g/ml.

The viscometer was calibrated with chloroform and acetone at 25 C. Viscometer constants were found to be C=4.134 x 10-2 and

E=1.495 x 10-5 in

$$\eta = Cdt + Edt^{-2} \qquad [30]$$

Run times in m-chlorophenol solutions were in the range of 12.5 to 20 minutes. The corrections from Edt-2 were negligible for this case.

Rum times of equivolumetric m-chlorophenol and trifluoroacetic acid were in the three to five minute range. Run times in pure trifluoroacetic acid were all under one minute, so the correction term was required.

Mark-Houwink constants found for Poly(etheylene terephthalate) in the literature [13-18] were used to approximate molecular weight of PDNBAT. These are listed on Table 31. The justification for this was the similarity in the molecular structure of the two polymers. The PDNBAT repeat unit is longer by N-(AR-NO2)-CH2-CH2. Dilute solution viscometry uses the volume of a molecule completely surrounded by solvent. So, the primary consideration is the molecular size. PET molecules coil much more easily and occupy less space than the PDNBAT molecules hindered with additional bulky nitrobenzene groups. Therefore,

the use of PET's constants approximates the molecular weight of PDNBAT on the low side. There are enough structural similarities between PET and PDNBAT so that the latter goes into all of the suggested PET solvents. Furthermore, three independent systems yielded the same range of the molecular weight. (See Table 31)

There were no reported constants for the 50/50 mixture of TFA and m-chlorophenol. Therefore, two sets of limiting values were used for the 50/50 mixture viscosities: PET in m-chlorophenol and PET in TFA. The intrinsic viscosities of PDNBAT in m-chlorophenol and PDNBAT in TFA yielded the same range of the molecular weight with the appropriate PET Mark-Houwink constants.

TABLE 31: APPROXIMATED MOLECULAR WEIGHTS OF PDNBAT

---Mv FROM THE ABSOLUTE VISCOSITY---
---TEREPHTHALOYL IN m-CHLOROPHENOL DATA---
---ALL USING PET K's and a's---

	K	a	50/50 IV25	RU	PURE m-CL-AR-OH IV9.3	RU	
25	0.0656	0.73	3432.9	10	885.86	3	12000-28000
3.3	0.93	0.77	6212.5	18	1720.0	5	------"------
	0.019	0.81	7093.2	20	2092.4	6	FRACTIONATED->
	0.017	0.83	6550.1	19	1989.9	6	8000-20000 Mv
	0.0425	0.69	10323.	29	2462.8	7	20000-150000

---TRIFLUOROACETIC ACID, INTRINSIC VISCOSITY = 18---

	K	a	PURE IV18	RU	50/50 IV25	RU
25 degr	0.14	0.68	1569.1	5	2581.2	8
30 degr	0.0433	0.68	7098.2	20	11506.	33

4879.9 <--AVERAGE
3312.5 <--DEVIATION
1367 4 <--RANGE +
7992.5 <--RANGE -

GENERAL DISCUSSION

SYNTHESIS CONDITIONS

It is very important to keep any water out of this type of step growth reaction. In the three discribed polymerizations diacid chlorides readily react with water to form diacids. The equilibrium constant for the ester formation from a diol and diacid is approximately one because the acids and esters are of approximately equal reactivity [36]. Therefore, there is only a small driving force for ester formation. This is not acceptable for higher molecular weight. Therefore, great pains were taken to keep the water out of the reaction. Dioxane was dried with sodium benzophenone. When there is no moisture present, sodium benzophenone turns the solution bright blue color. Triethyl amine was also rigorously dried. All liquid diacids were purified by distillation, and added to the reaction mixture under argon.

Another important factor controlling molecular weight of a polymer in step growth reactions is its solubility. This was the

major reason for the low molecular weight of the polymers. MAlonyl and terephthaloyl polymers precipitated at too low a molecular weight. This diffusion controlled reaction slows down to a stop in the solid state. Attempts were made to achieve a higher molecular weight in boiling dioxane, but the results were not drammatic.

A better solvent, trifluoroacetic acid, was found for PDNBAT. Higher molecular weight can perhaps be achieved in this system. In a strong acid, acid chlorides might form anhydrides, and diols form monofunctional esters. The esters are fairly slow-reacting, but strong acid anhydrides are good nucleophiles. So a step growth reaction, even with side reactions should yield a higher molecular weight.

It was ascertained that TFA does not degrade the polymer by cleaving the esters. The same viscosities were achieved from the polymer collected from TFA and pristine polymer.

Finally, melt polymerizations proved to be worse than solution method in terms of purity and molecular weight.

CRYSTALLINITY

The fact that PDNBAM and PDNBAT are completely amorphous is easily explained by examination of conditions of polymer crystallinity. The major requirement for crystallinity is a regularity and symmetry of a repeat unit. The polymers with smaller and linear repeat units crystallize much easier than their counterparts with longer repeat units and bulky side groups. Also, the axial symmetry of pendant groups with respect to the polymer backbone plays a big role in the polymer crystallinity.

This can be demonstrated by the effect that R groups have on crystallinity of PET derived polymers in

$-(O_2C-C_6H_4-CO_2-R)-$ [34]

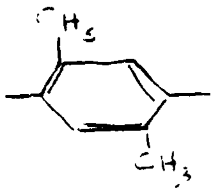
TABLE 32

R	Tm (^{o}C)
$-CH_2CH_2-$	265
$-CH_2CH_2CH_2-$	220
$-CH_2-CH(CH_3)-$	NONCRYSTALLINE
$-CH_2CHCH_2-$	NONCRYSTALLINE

CH_3 $-CH_2CH_2CH-$ CH_3	NONCRYSTALLINE
CH_3 $-CH_2-C-CH_2-$ CH_3	140

and in

$-(O_2C-R-C-O_2-CH_2-CH_2)-$



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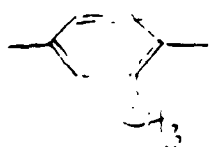

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This is a major effect contributing to the lack of crystallinity of the discussed polymers. Another, lesser effect might be associated with the tacticity of the amine group in the polymers. Vinyl polymers, such as PVC demonstrate the effect of tacticity on the crystallinity. If PVC is atactic, it

is completely amorphous, but isotactic PVC is crystalline.

In this work, all of the polymers contain three bulky substituents on the amine. Two of them are the polymer chain, the third is nitrobenzene. If the tacticity of the nitrobenzene group and the lone electron pair along the polymer chain is examined, it is easily seen that several configuration are possible: atactic, isotactic and syndiotactic. In all three polymers the tertiary amine is not purely tetrahedral, it has some aromatic character due to the resonance with the nitro-benzene group.

It is well known that sterrically nonhindered amines rapidly undergo tacticity inversions [35]. The rotation is so fast that only the average configuration is seen. As a result, aniline molecule will appear planar, and upon crystallization a molecule will "wait" for the needed confirmation of the amine group. Such tacticity inversion is strongly sterrically hindered in the discussed polymers. Here, the configuration is permanent. As a result, these polymers can be viewed as atactic, inhibiting crystallinity. This is a very small effect, because the nitro-benzene groups are so far removed.

SECOND HARMONIC GENERATION

EXPERIMENTAL

PDNBAM and PDNBAT films were cast from solution on a In doped SnO glass. These films were poied above their respective Tg's for 30 to 60 minutes at 2-20 MV/cm. An aluminum lead was attached to the polymer surface and a DC current was passed from a battery. The film acted as a capacitor between two conducting plates (In doped SnO glass and Al). The sample was placed into a furnace mantained at temperature above the polymer's Tg. The voltage drop across the film was monitored with a voltmeter. Thicknesses were measured on a Dektak film thickness analyzer. The thicknesses ranged between 0.1 to 0.5 microns. The polymer from sebacoyl chloride was not used because of its low glass transition temperature.

The films were subjected to Nd+++/YAG laser (wavelength = 1.064 micron). If SGH was to be observed a green beam of light (wavelength 0.532 micron) would have been produced. However, the

polymer samples only fluoresced at high intensities, emitting no beam.

DISCUSSION AND PROPOSED IPROVEMENTS

Poling a polymer film above its Tg at high voltages and rapidly cooling it to room temperatures "freezes in" aligned active groups [19-23]. Voltages of the order of megavolt/cm readily orient polar nitro-aniline moieties in the polymer chain.

The lack of the second harmonic generation in the poled polymer films shows a need for further study and optical characterization of these polymers. Some of the questions that have to be answered are:

1) What is the thickness range of the film for optimal SGH?

It is obvious that there exists a minimal thickness of the poled polymer film, below which no SGH can be easily detected. On the other hand, there is a maximum thickness beyond which the signal intensity loss is too great.

2) What is the minimal necessary voltage for poling of these films?

It is also clear that for different voltages, there are different degrees of the polymer orientation, and thus, different

degrees of the active group allignment. Maximum orientation is desired, but at higher voltages, the polymer degrades.

3) What are the implications of the amorphous state on SGH?

In a non-centrosymmetric crystal, the incident light beam must be phase matched with the produced half-wavelength light for amplification of the signal. Proper orientation of the crystal insures that the two signals will travel in phase and at the same speed. However, it is not clear what constraints this puts on a poled amorphous film with regard to the SGH detection.

As a reference, SGH measurements of poled nitroaniline impregnated in PMMA will be carried out. Nitroaniline has a strong dipole moment (6.22-6.7) [26-28], but due to its centro-symmetric crystalline structure exhibits no SGH [38].

4) What is the variation of quadratic hyperpolarizability with the different concentrations of optically active groups in the polymer.

PDNBAS has 1 active group per every 17 backbone atoms, PDNBAT has 1 active group per every 13 atoms, and PDNBAM has one active group per every 10 backbone atoms. Obviously, the optimal case is for every atom in the chain to be active, but it is not a trivial synthetic task to optimize this density.

5) An interesting question arises if polymer crystallinity is

achieved. Unless a single polymer crystal is grown, some amorphous regions will exist. These regions will be oriented via poling, but the poling angle must match the optical orientation of the crystal for the phase matching. So it might be necessary to pole a polymer film at odd angles. It is not clear at present how this can be done.

It is certain that higher molecular weight is necessary for for better mechanical properties of polymers. The brittleness of the thin films indicates that these systems are not commercially usable at present. The arising question is: how does the molecular weight influence properties like melting point and glass transition point of polymers? A literature survey [1-8] for PET produced the data appearing in Figure 20. Here, the melting point of PET was plotted vs number of the repeat units or degree of polymerization of the oligomer/polymer. The graph shows that melting temperature becomes independent of the molecular weight of the polymer after polymer length of 5-6 repeat units. Dicarboxilic acid data were not used in this Figure because of the chain end influence on crystallization in these materials. So, if crystallinity is achieved for these systems, the molecular weight

influence on the melting point will not be great outside of the oligomeric regime.

However, PET shows strong dependence of the glass transition temperature [9] on the molecular weight until the molecular weight is 9,000-10,000 or DP>50 (Figures 21 and 22). Here the molecular weight was calculated using reported Tg variation with the intrinsic viscosity. This data were converted to molecular weight of PET using reported Mark-Houwink constants.

Since the molecular weight of PDNBAT was estimated at 5,000, the average number of repeat units is 14, and the conversion is roughly 92%. A molecular weight of 5000 +/-2000 places this polymer on the almost linear ramp of the curve in Figure 22. Therefore, it is very likely that the glass transition range of these polymers can be raised by as much as 25 degrees.

Such wide range of possible molecular weights of the polymers demonstrates a need for absolute molecular weight measurements, such as light scattering and freezing point depression. No such equipment is readily available at present, but efforts are under way to measure the molecular weight via an absolute technique elsewhere.

After better solvents for polymerization are found, it will

be highly educational to reproduce Figures 21 and 22 for PDNBAT and PDNBAM and calculate Mark-Houwink constants for these polymers.

It is very desirable to produce new, more aromatic and crystalline polymer system with a higher active group concentration. Strategic aromaticity of the backbone will insure ridgidity of the polymer and perhaps yield liquid crystallinity. This is desirable for the earlier discussed reasons.

FIGURE 1. Infrared Spectra of [illegible]

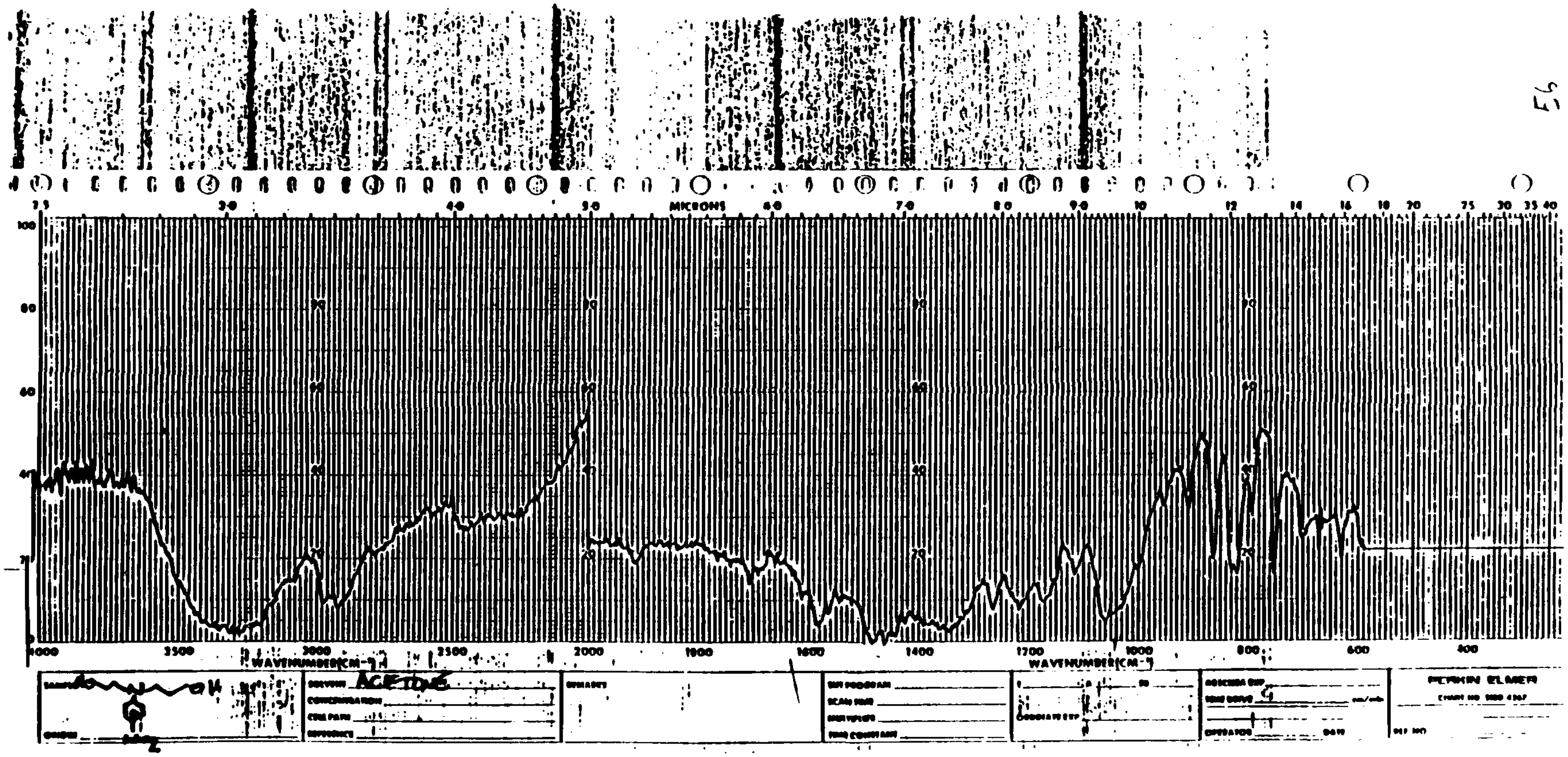
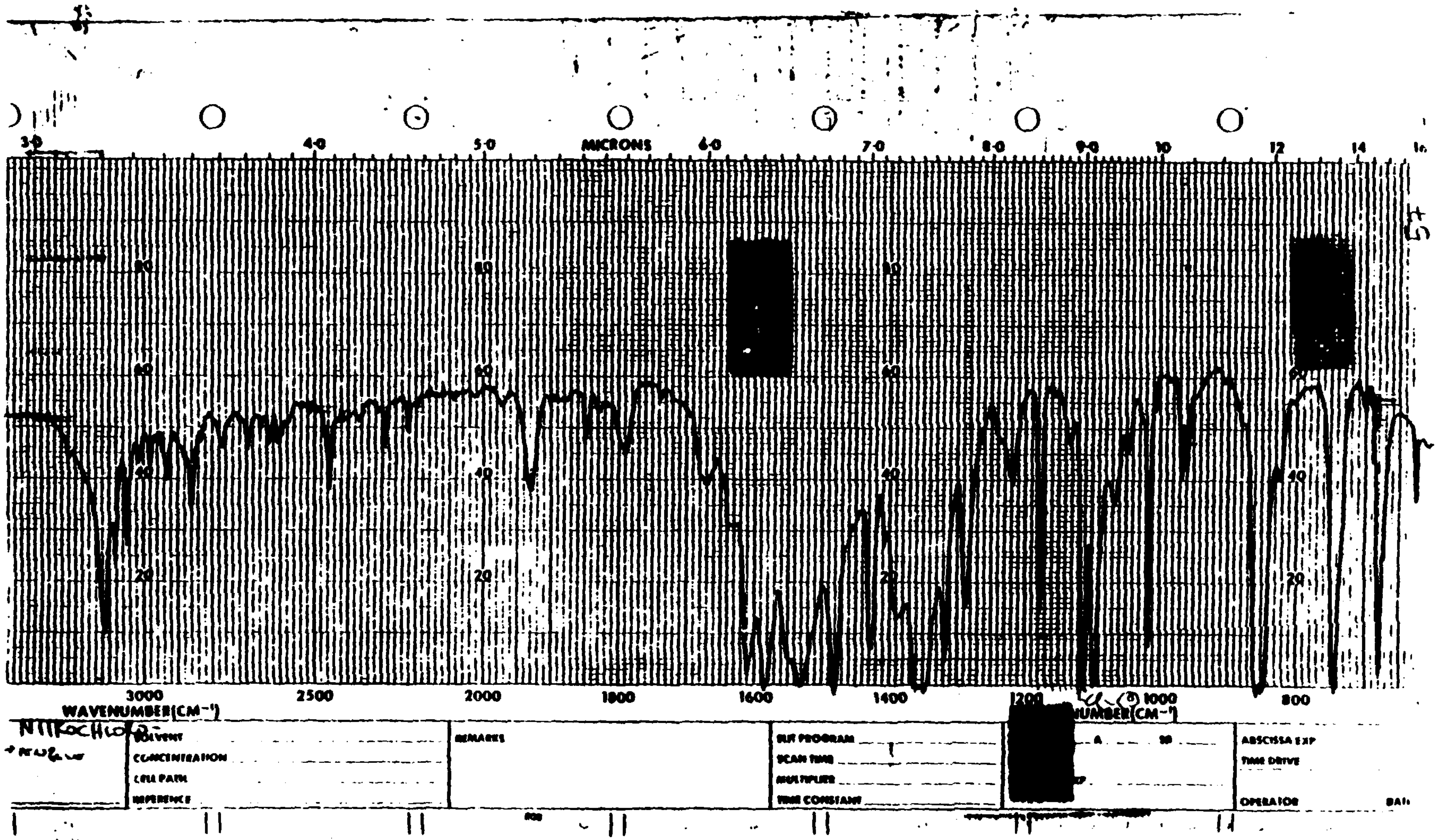


FIGURE 1a: Infra-red spectra of p-chloro-nitrobenzene



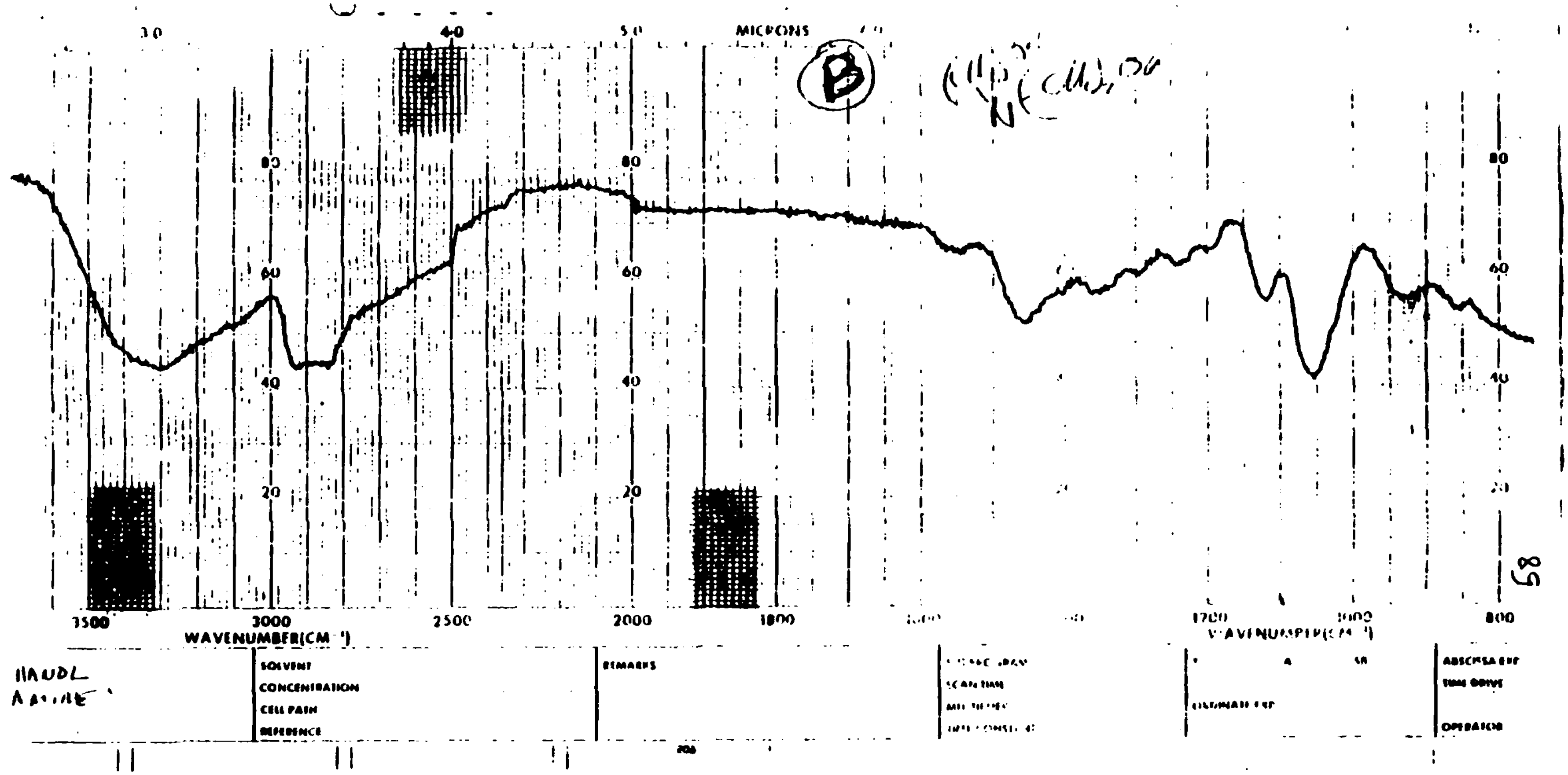


FIGURE 1c: Infra-red spectra of diethanol amine

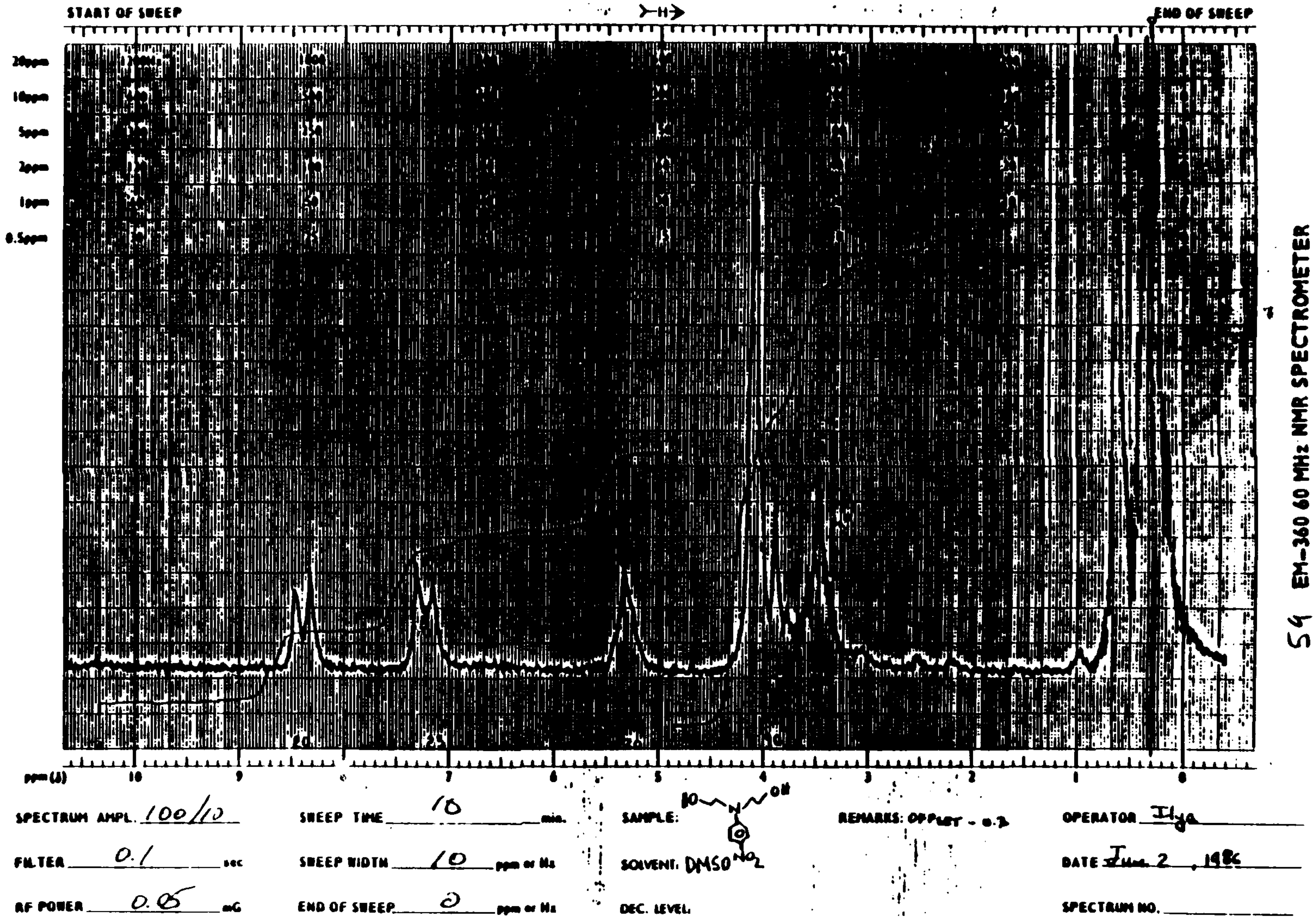


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FIGURE 2: NMR spectra of N,N-diethanol-4-nitrobenzenamine

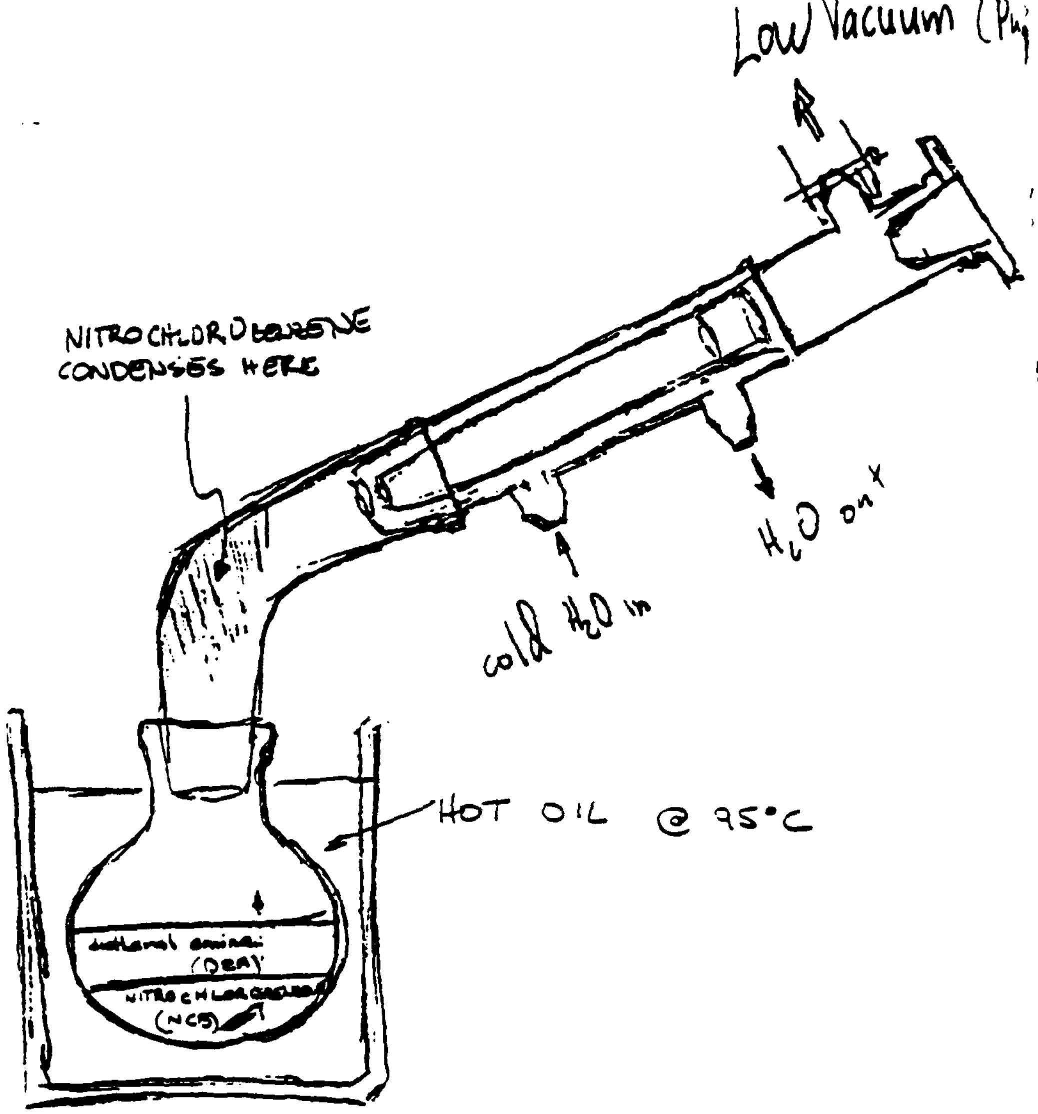
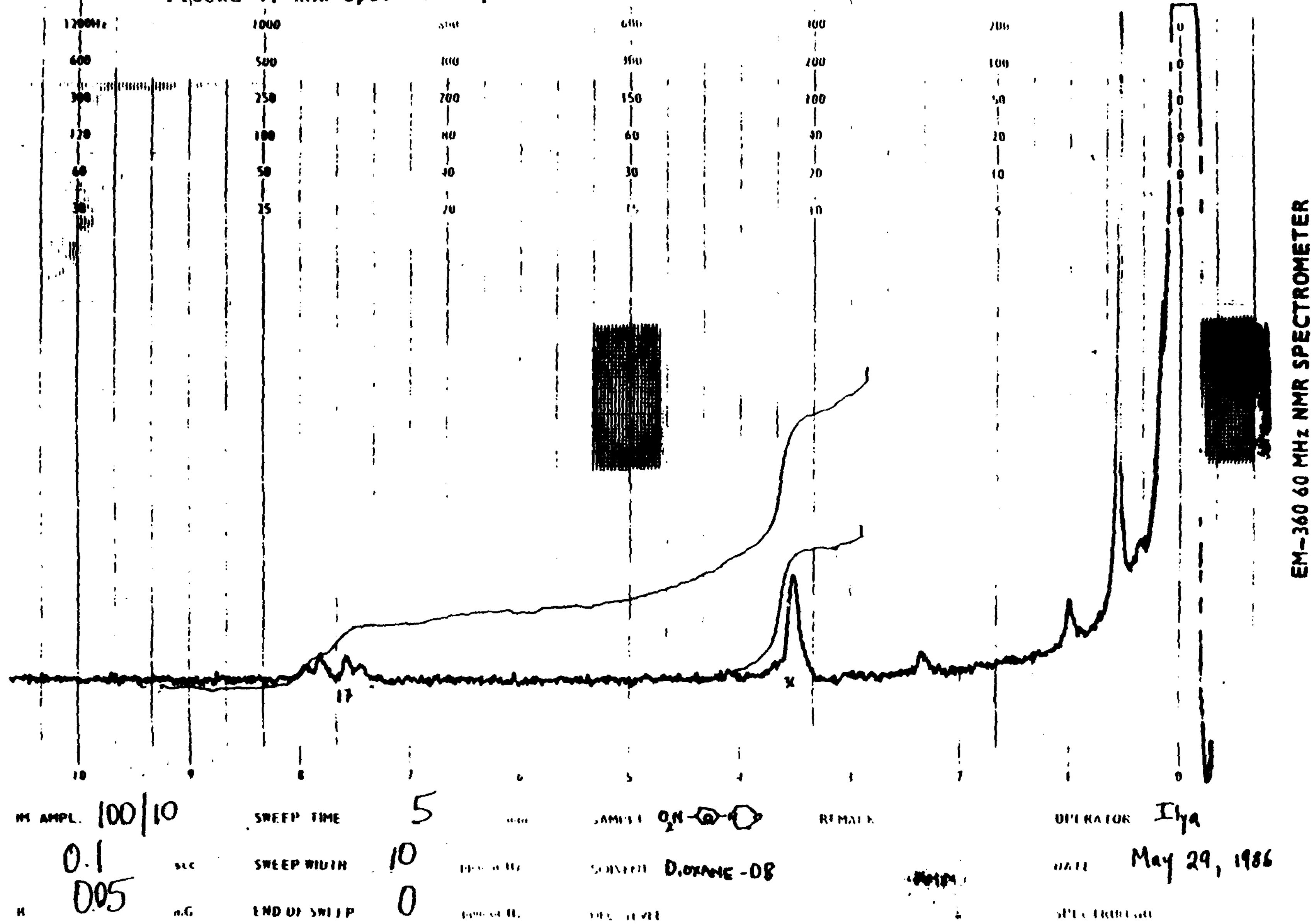


Figure 3: Removal of Nitrochlorobenzene

FIGURE 4: NMR spectra of p-nitro-benzoxazine



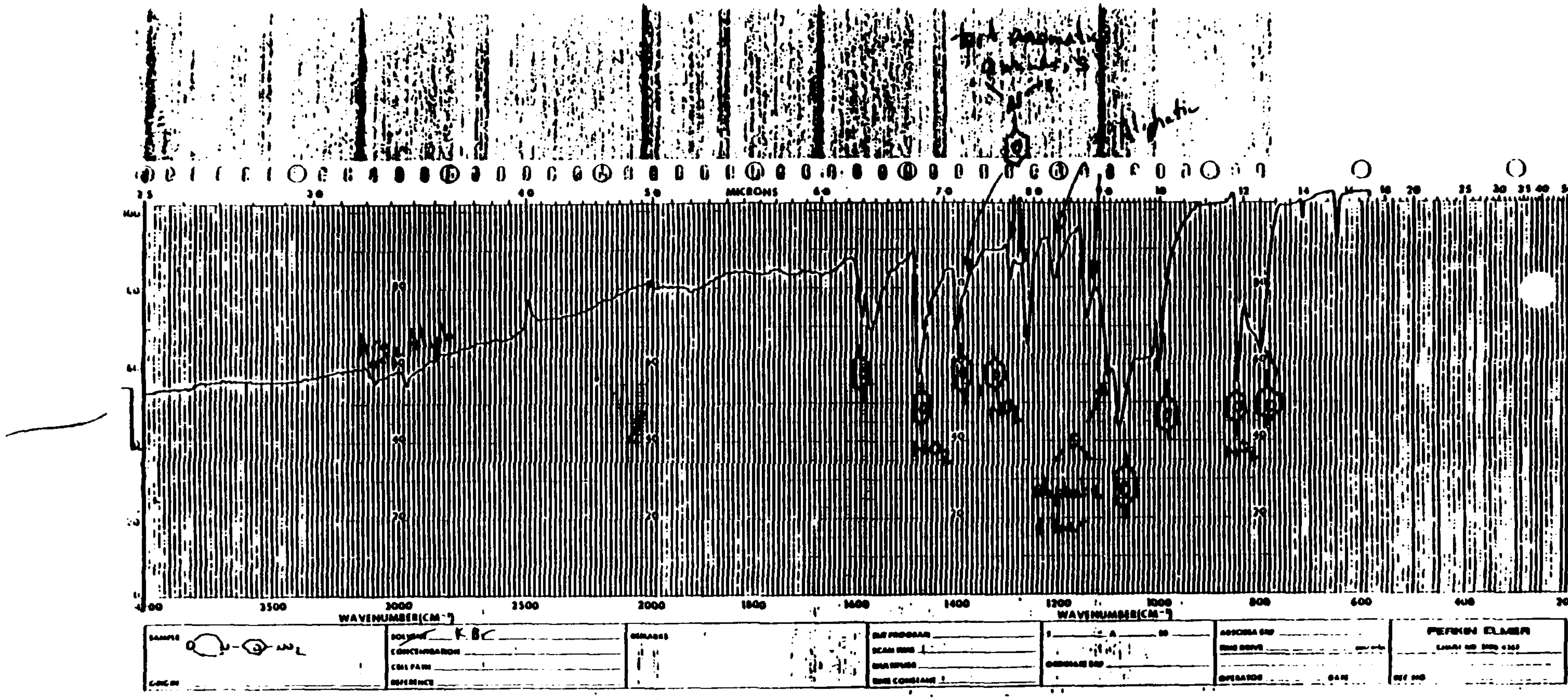


FIGURE 5: Infra-red spectra of p-nitro-benzoxazine

[redacted]

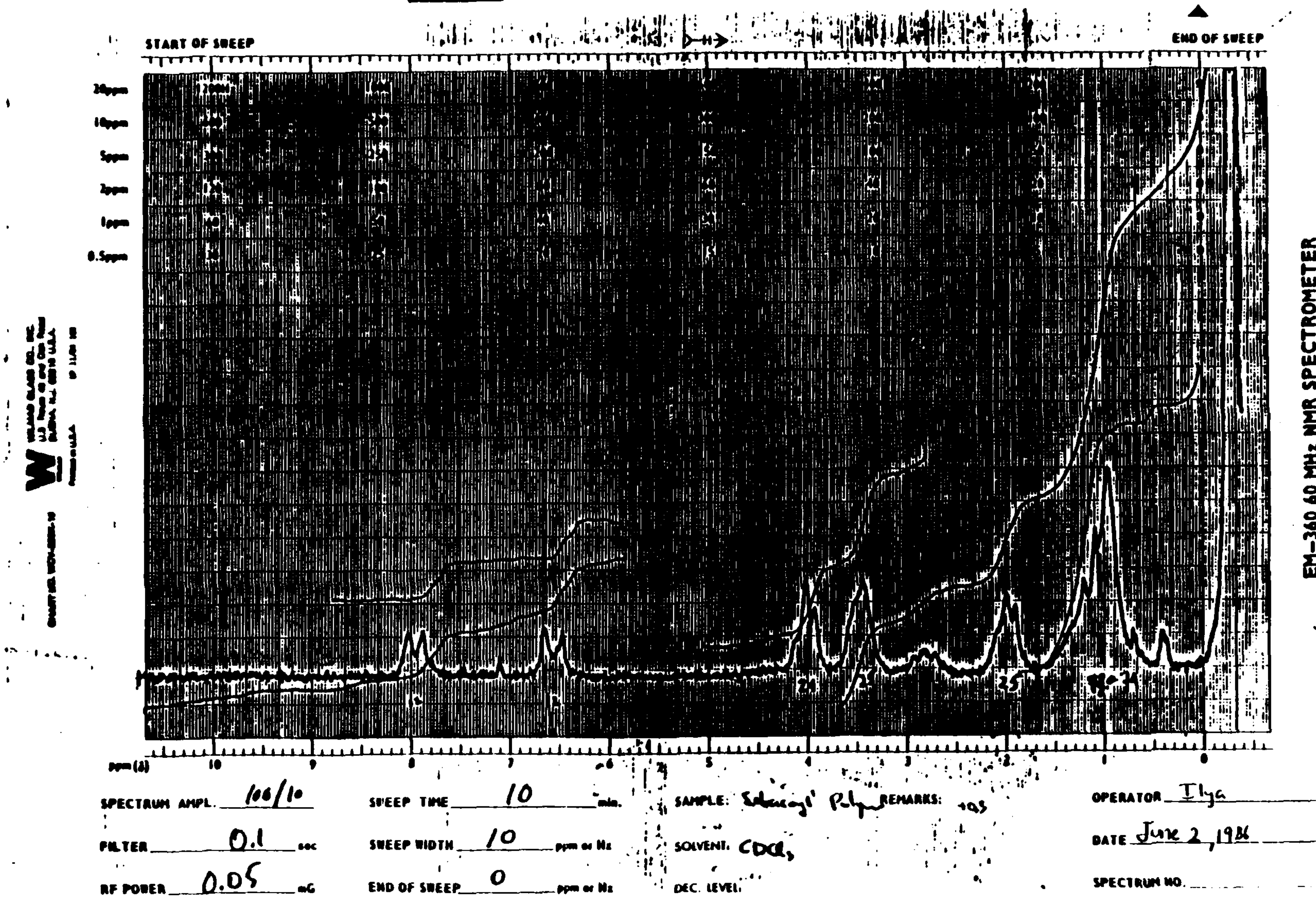
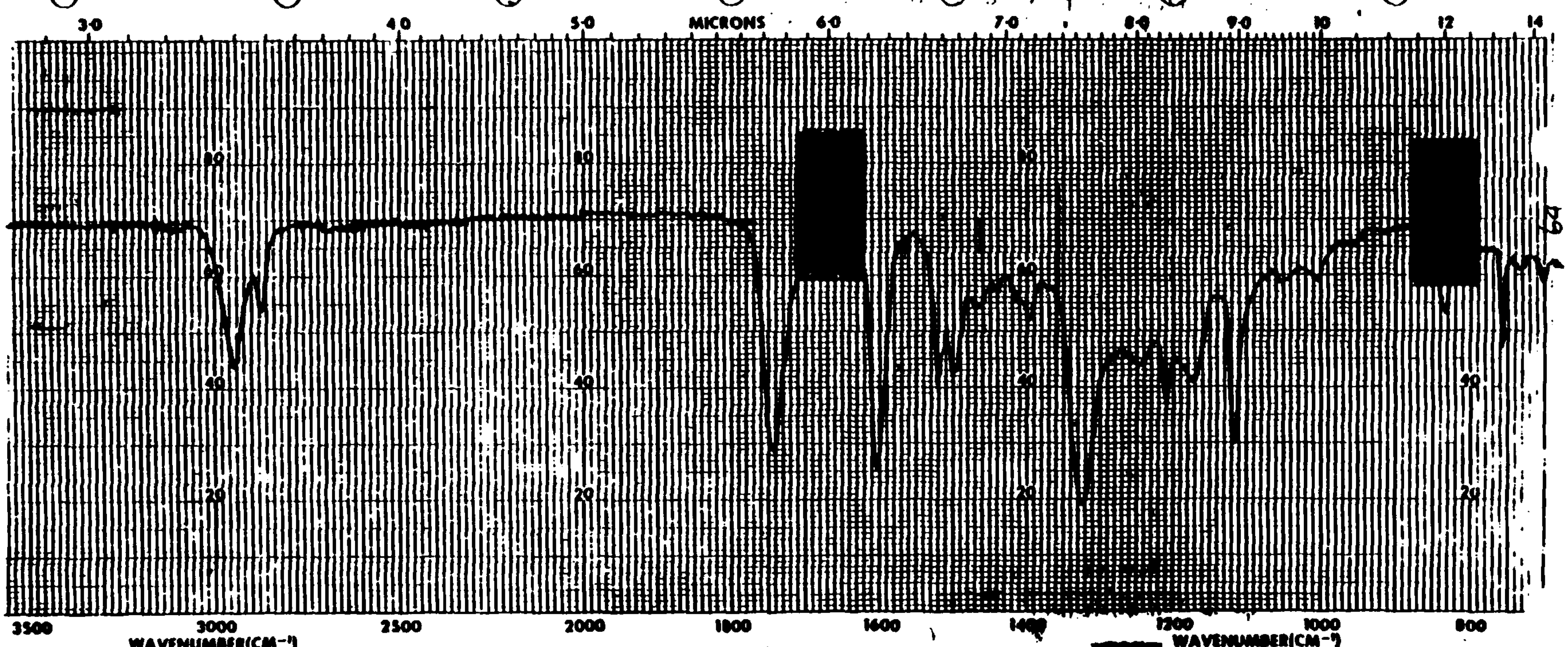


FIGURE 6: NMR spectra of PDNBAS



SEBACOYL POLYMERS	SOLVENT Acetone CONCENTRATION CELL PATH REFERENCE	REMARKS	SLIT PROGRAM [redacted] A 88 SCAN TIME MULTIPLIER ORDINATE EXP TIME CONSTANT	ABSCISSA EXP TIME DRIVE OPERATOR

[redacted]

[redacted]

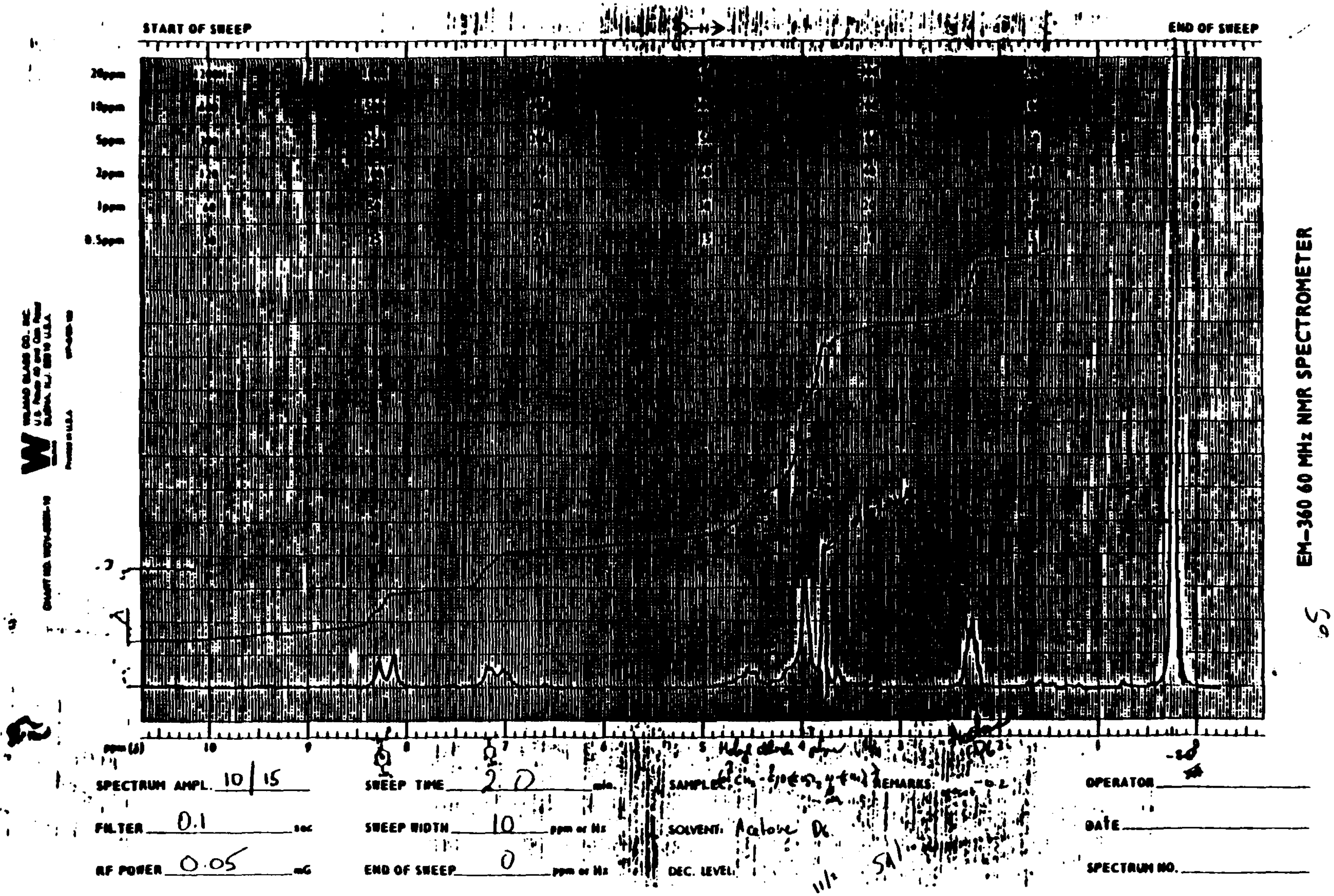


FIGURE 8: NMR spectra of PDNBAM

[redacted]

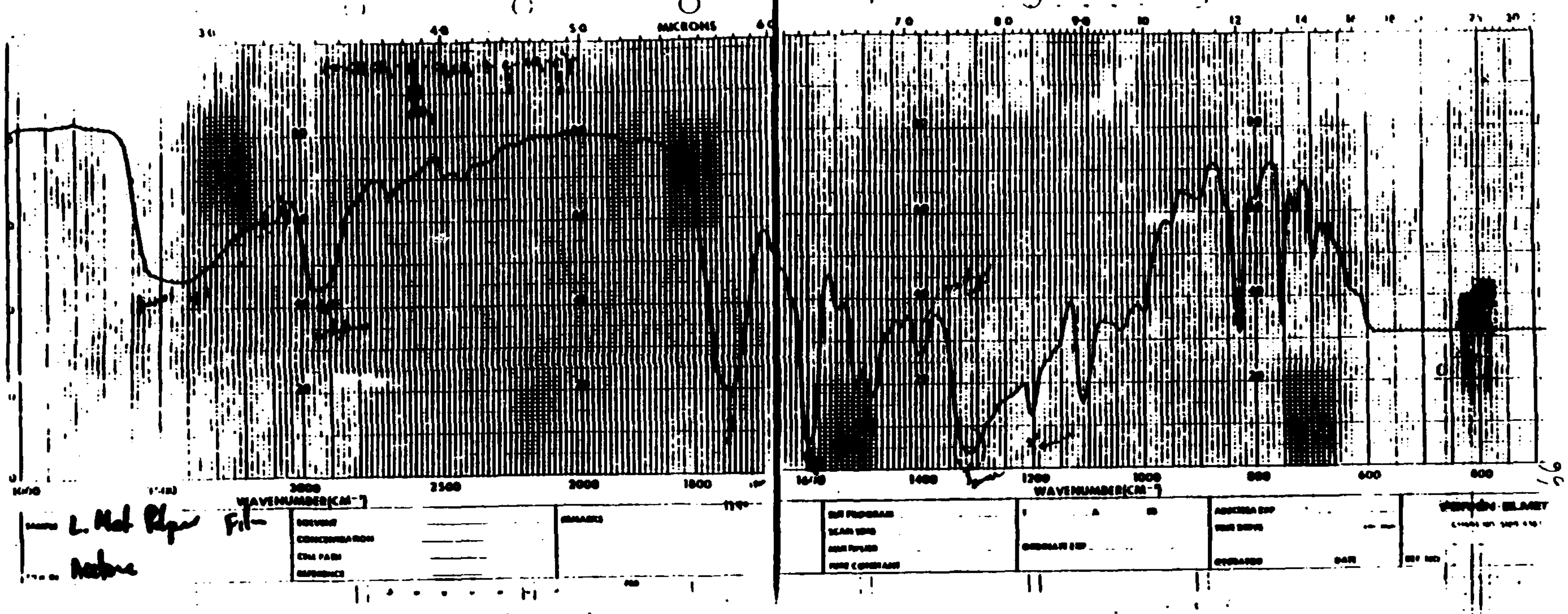
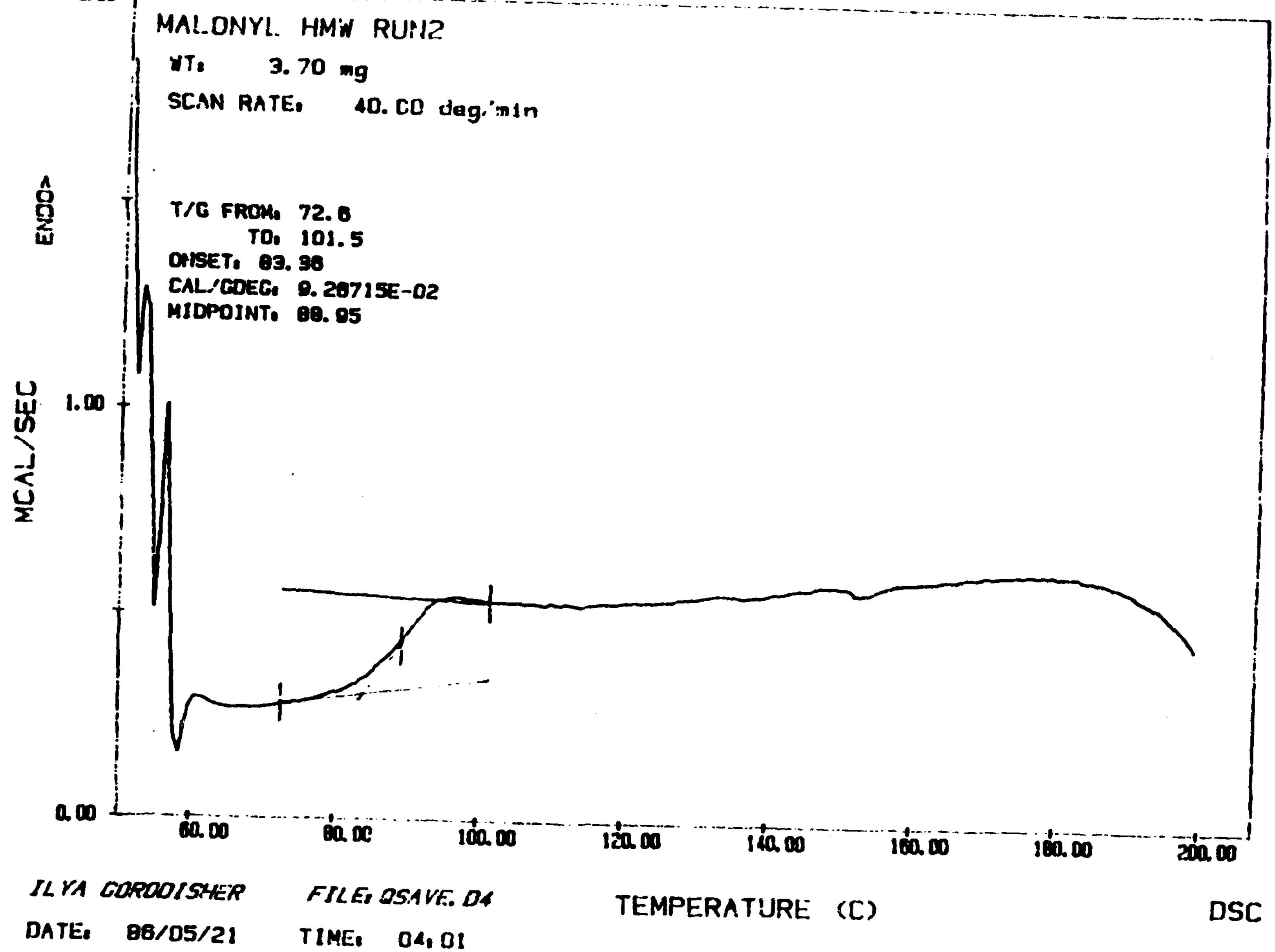


FIGURE 9: IR spectra of PDNBAM

FIGURE 10: DSC of PDNBAM



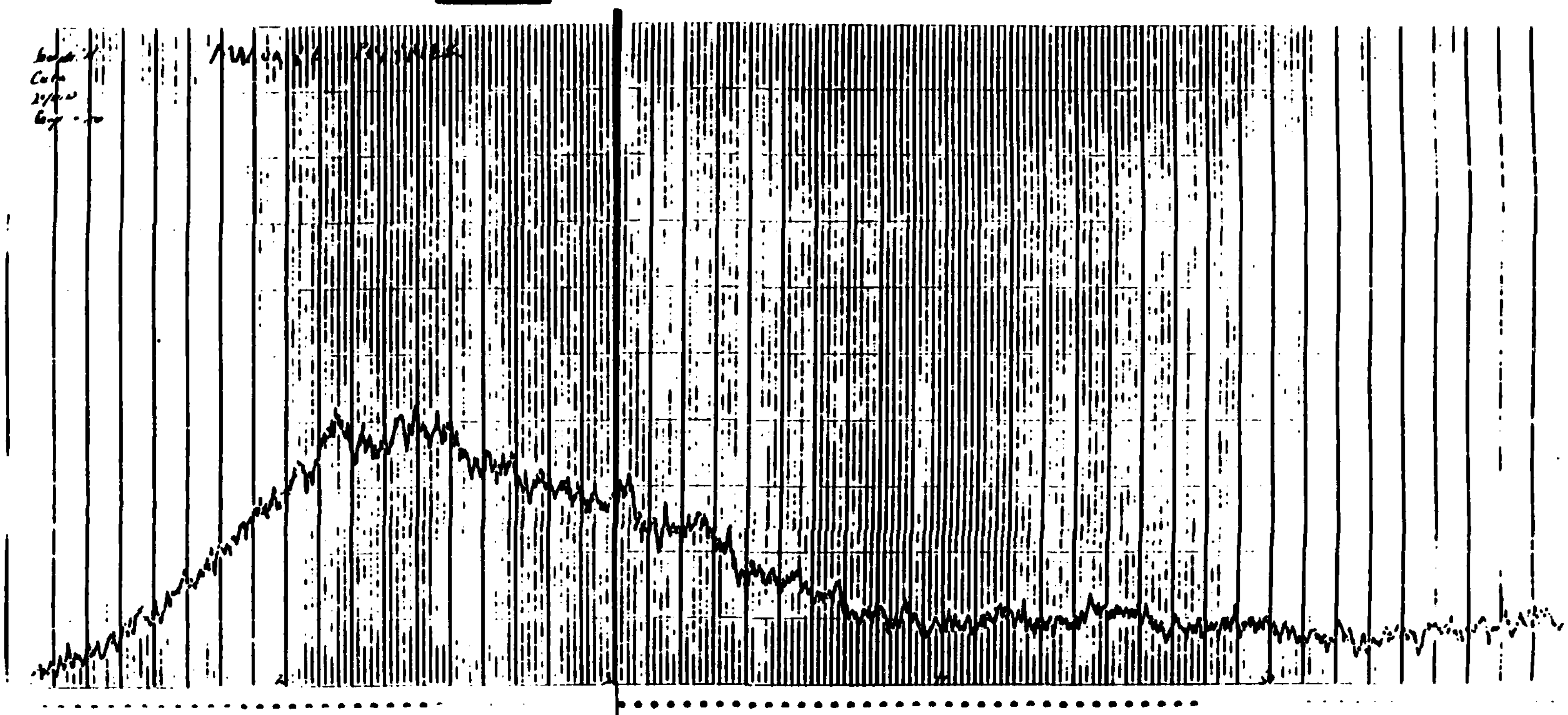
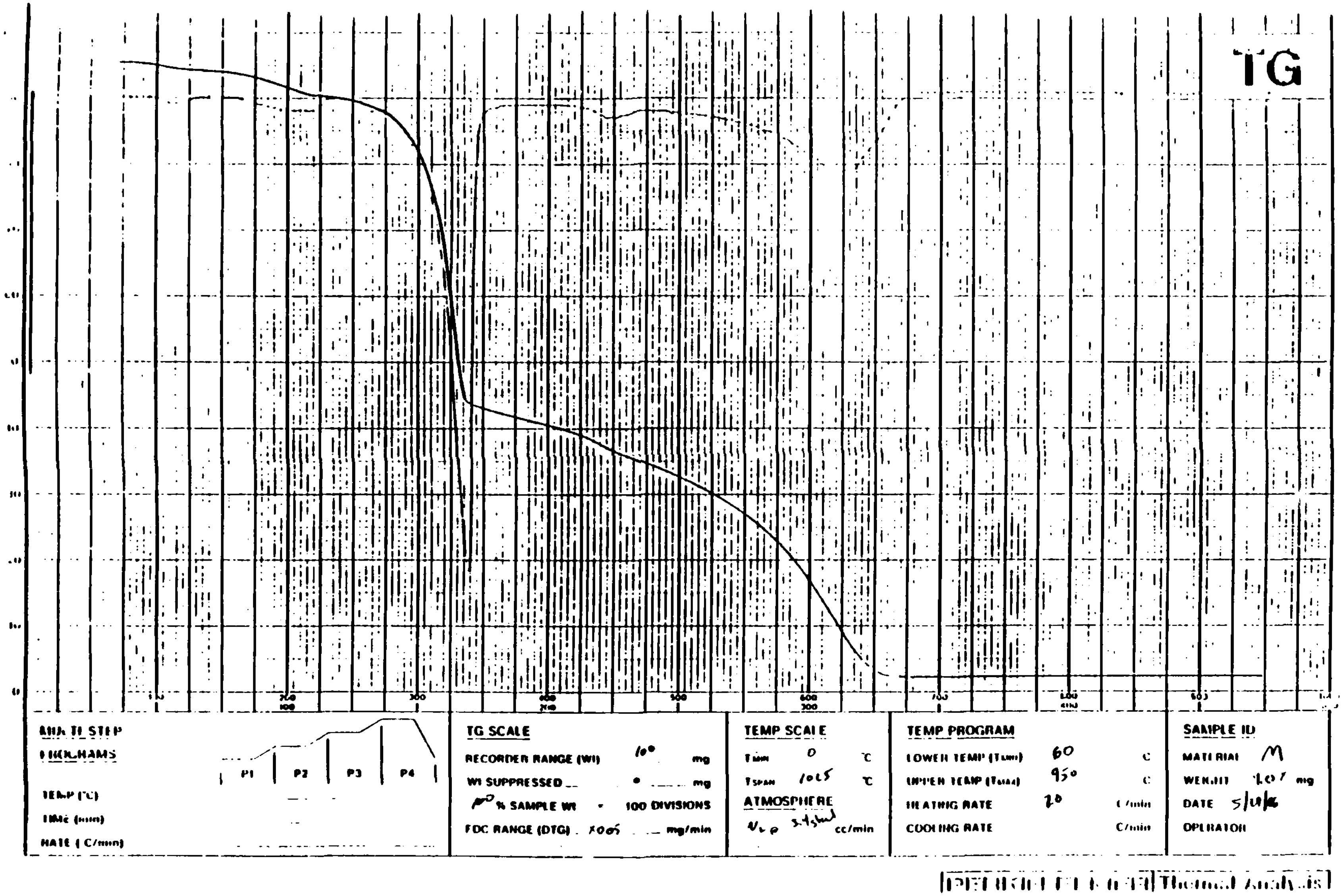


FIGURE 11: X-ray diffraction spectra of PDNBAM

FIGURE 12: TGA of PDNBAM



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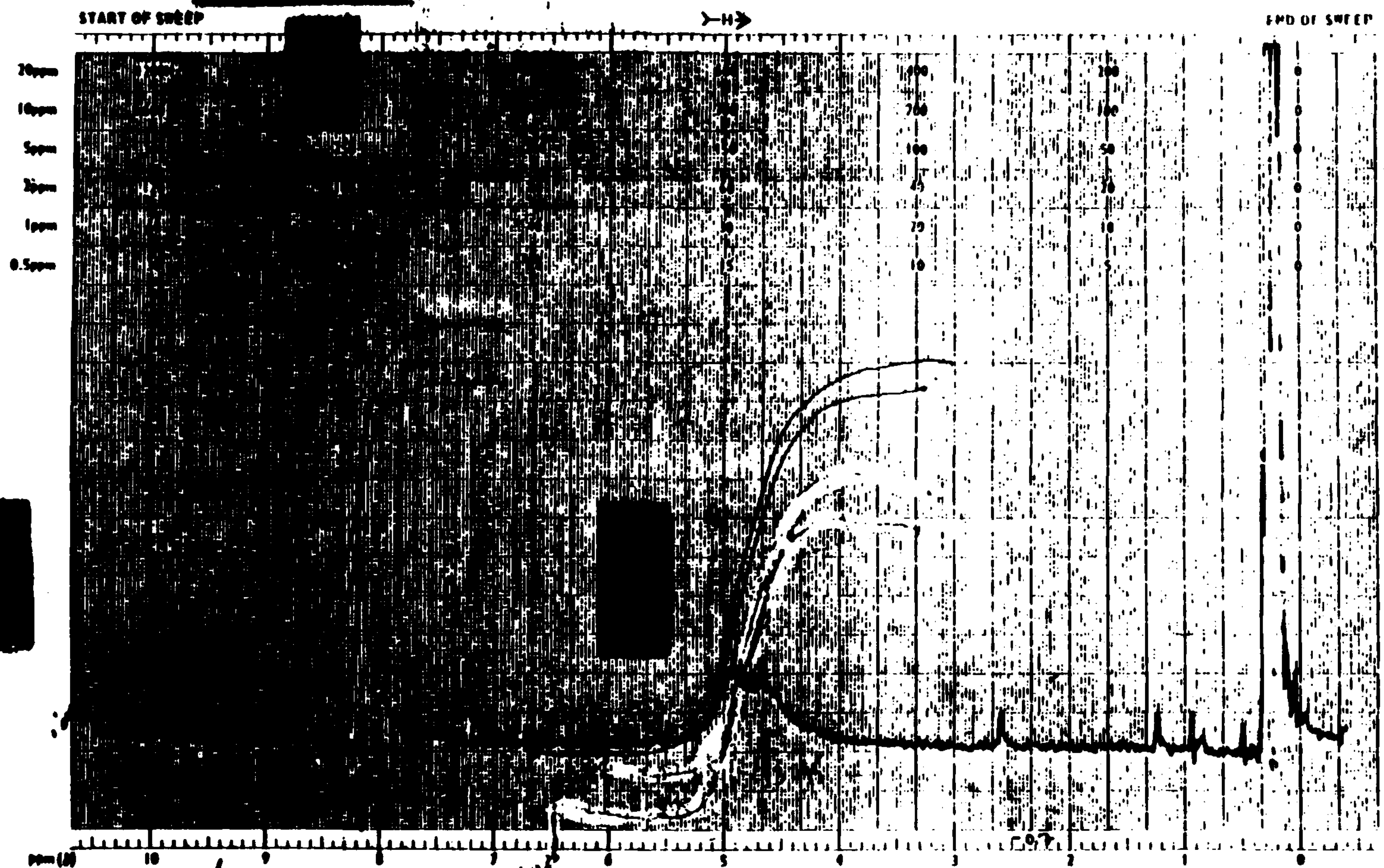


SPECTRUM AMPL. 100/7.5 SWEEP TIME 5 min SAMPLE: Terephthaloyl polymer REMARKS EXTERNAL TMS 0.2 offset OPERATOR

FILTER 0.1 sec SWEEP WIDTH 10 ppm or Hz SOLVENT CF_3COOH DATE 5/23

RF POWER 0.5 mG END OF SWEEP 0 ppm or Hz DEC. LEVEL SPECTRUM NO.

FIGURE 13: NMR of PDNBAT

FIGURE 14: IR spectra of PDNBAT

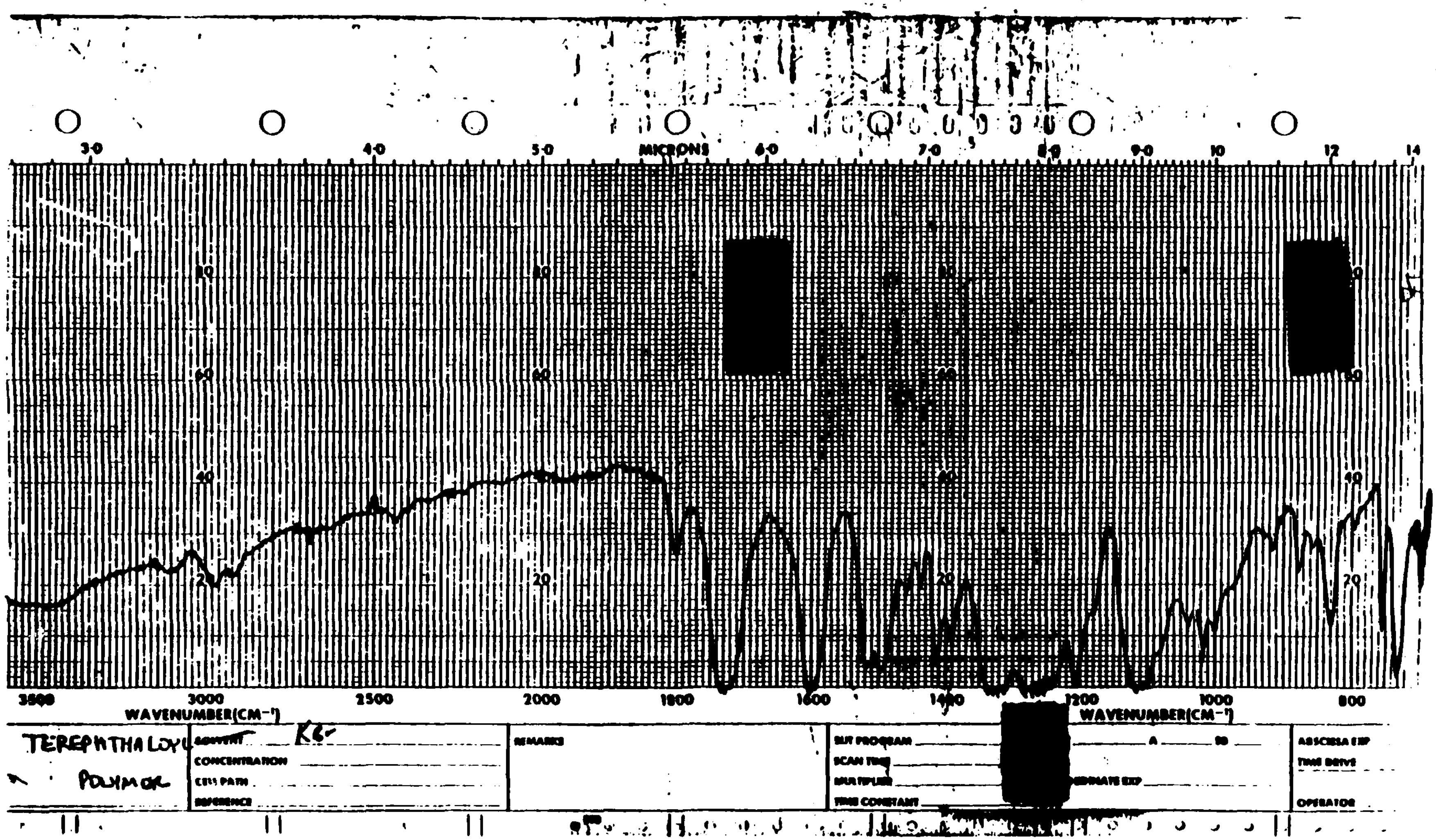
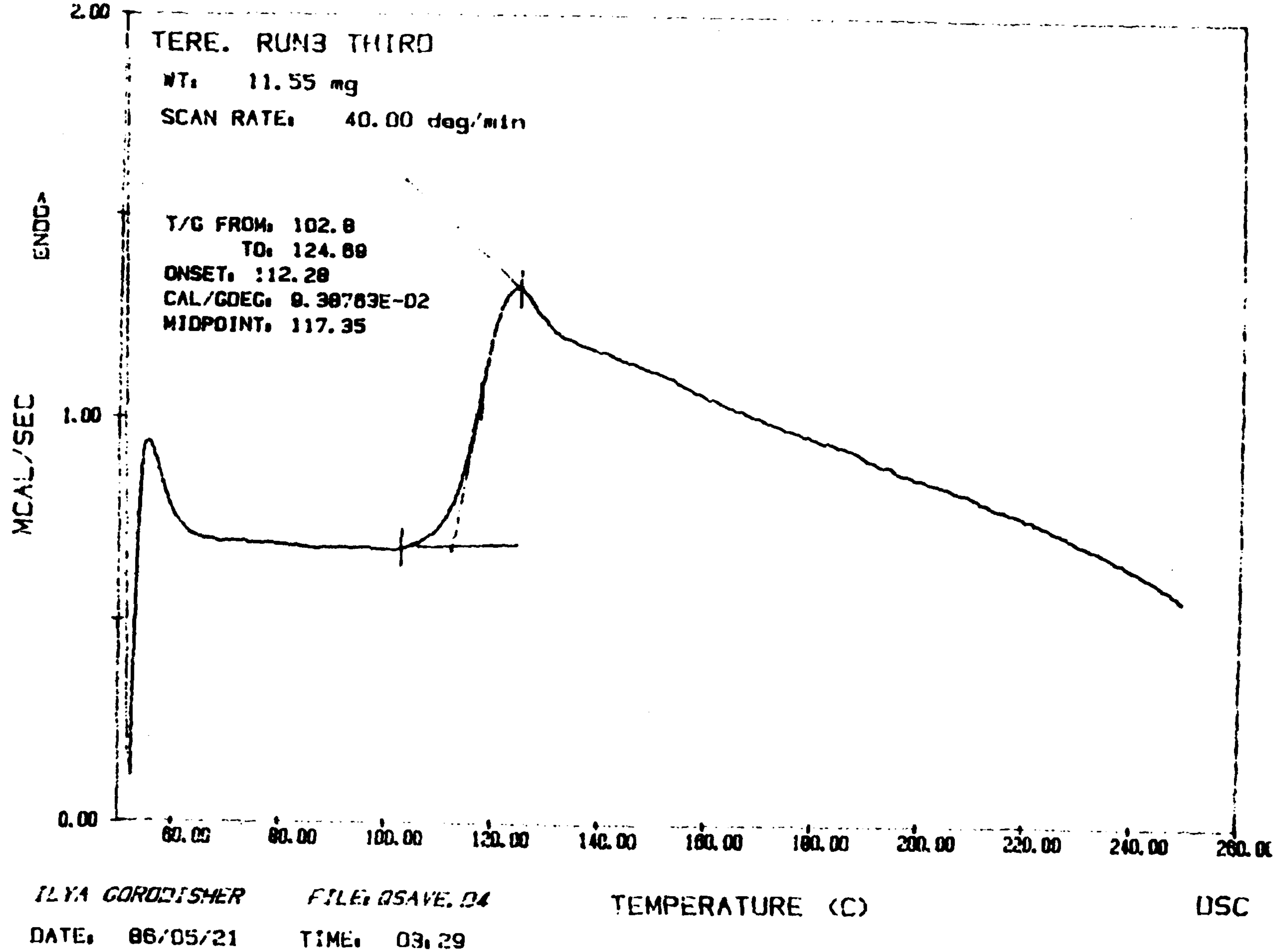


FIGURE 15: DSC of PDNBAT



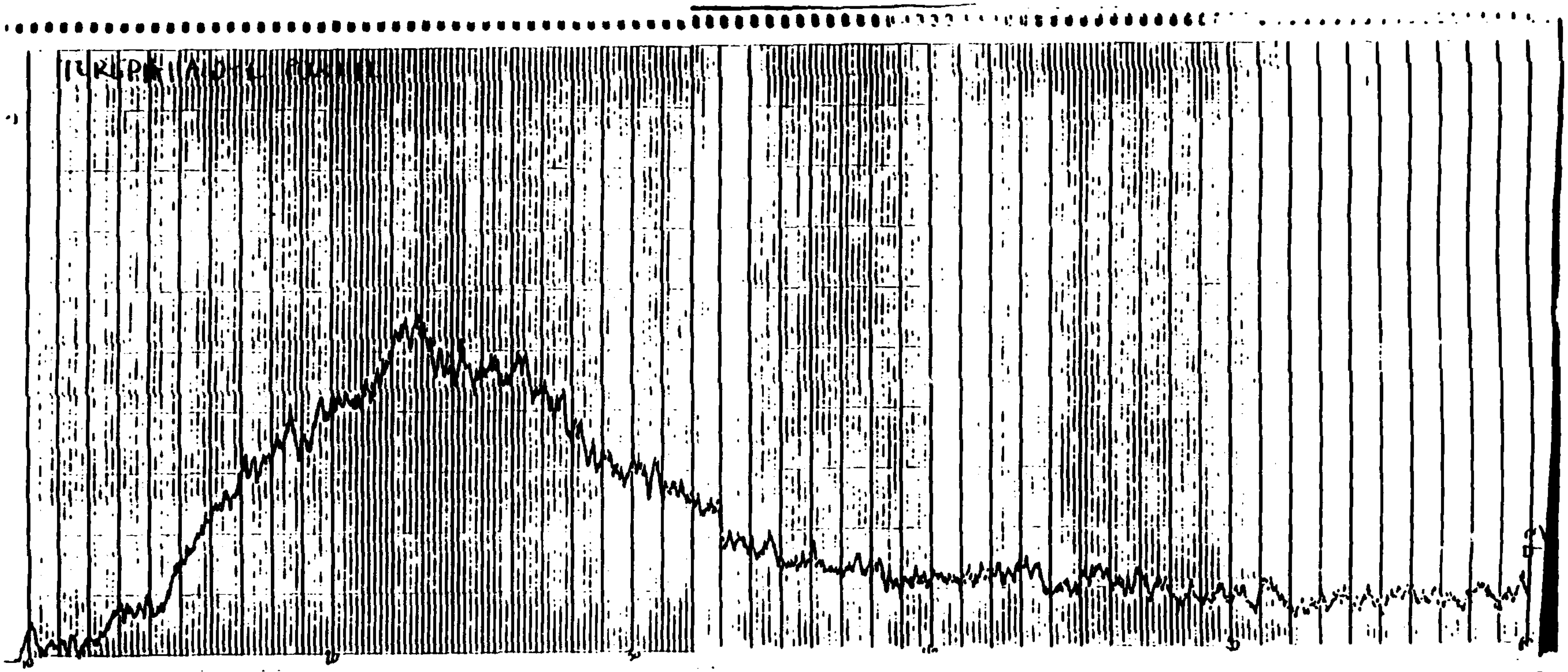


FIGURE 16: X-ray diffraction spectra of PDNBAT

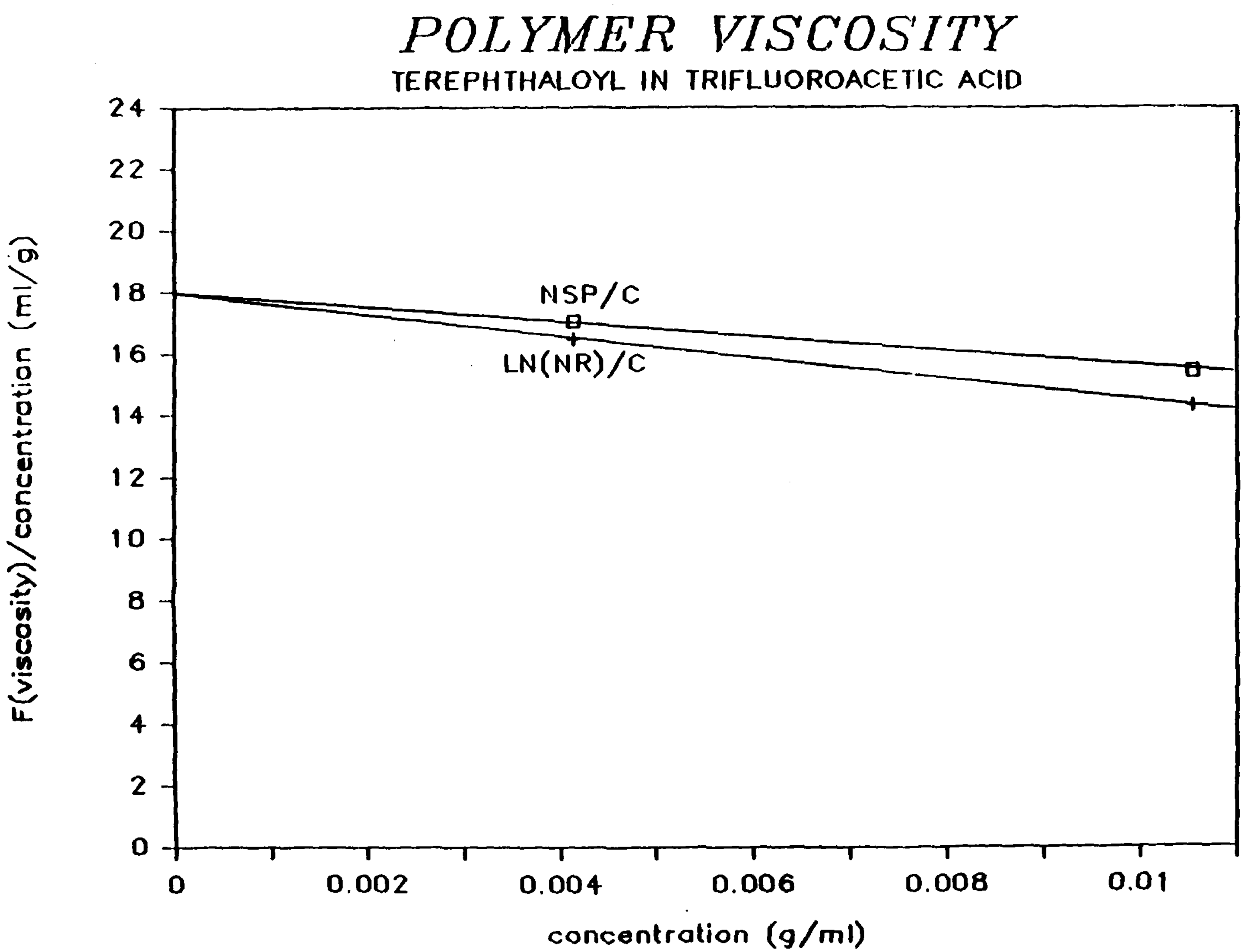


FIGURE 14: Extrapolated viscisities of PDNBAT in TFA

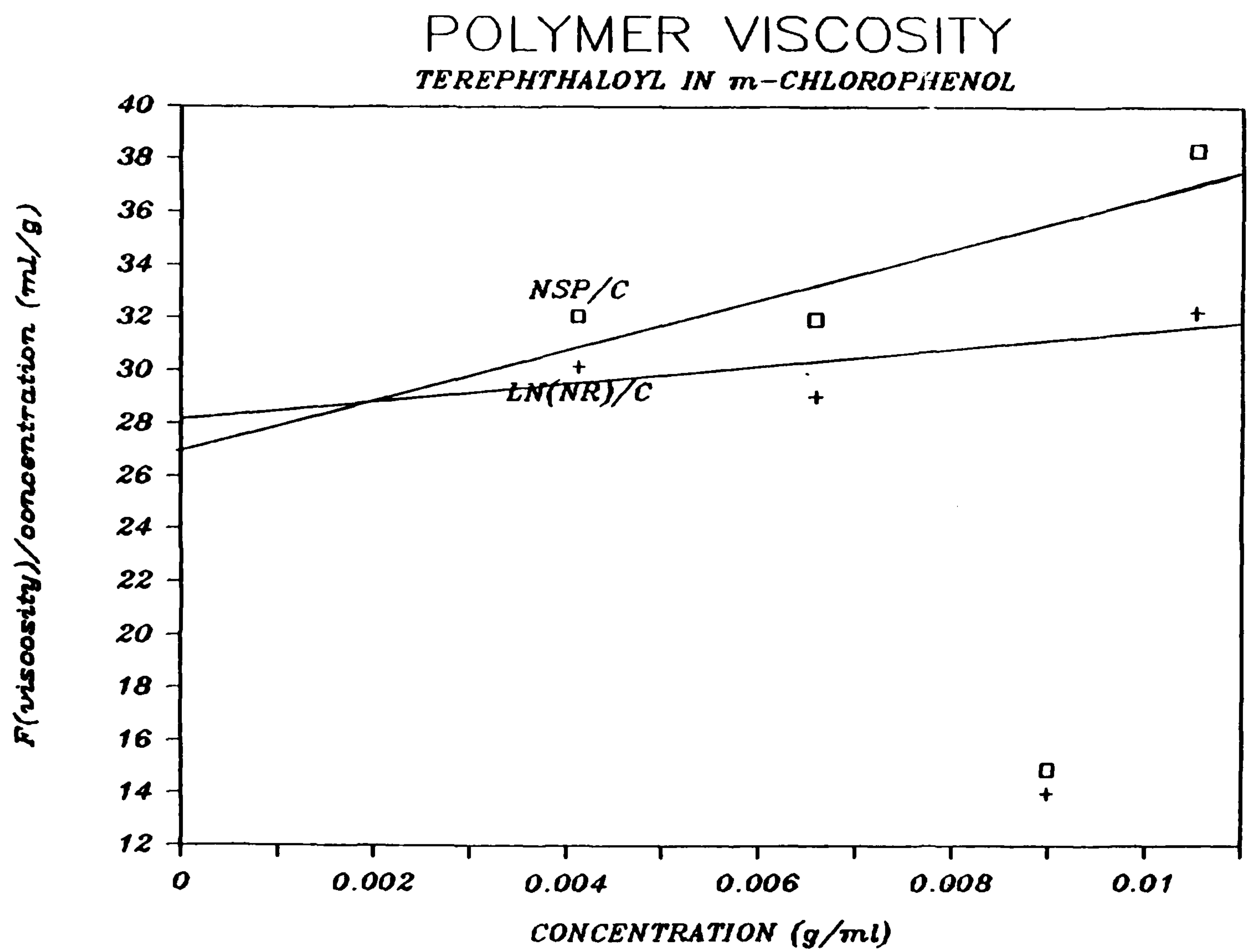


FIGURE 13: Extrapolated viscosities of PDNBAT in m-chlorophenol

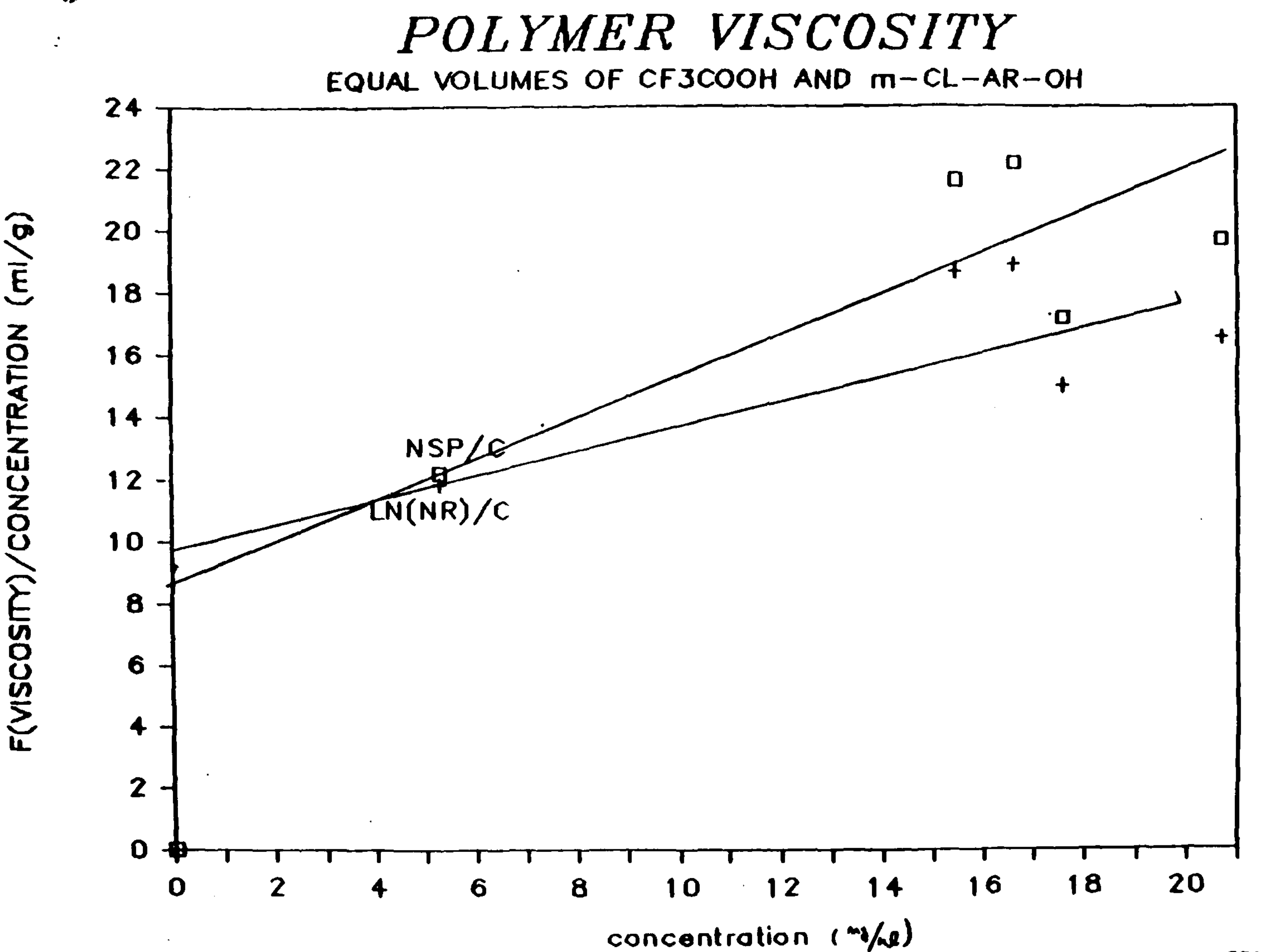


FIGURE 19: Extrapolated viscosities of PDNBAT in 50/50 mixture of TFA and m-CPh

PET: MOLECULAR WEIGHT vs Tm

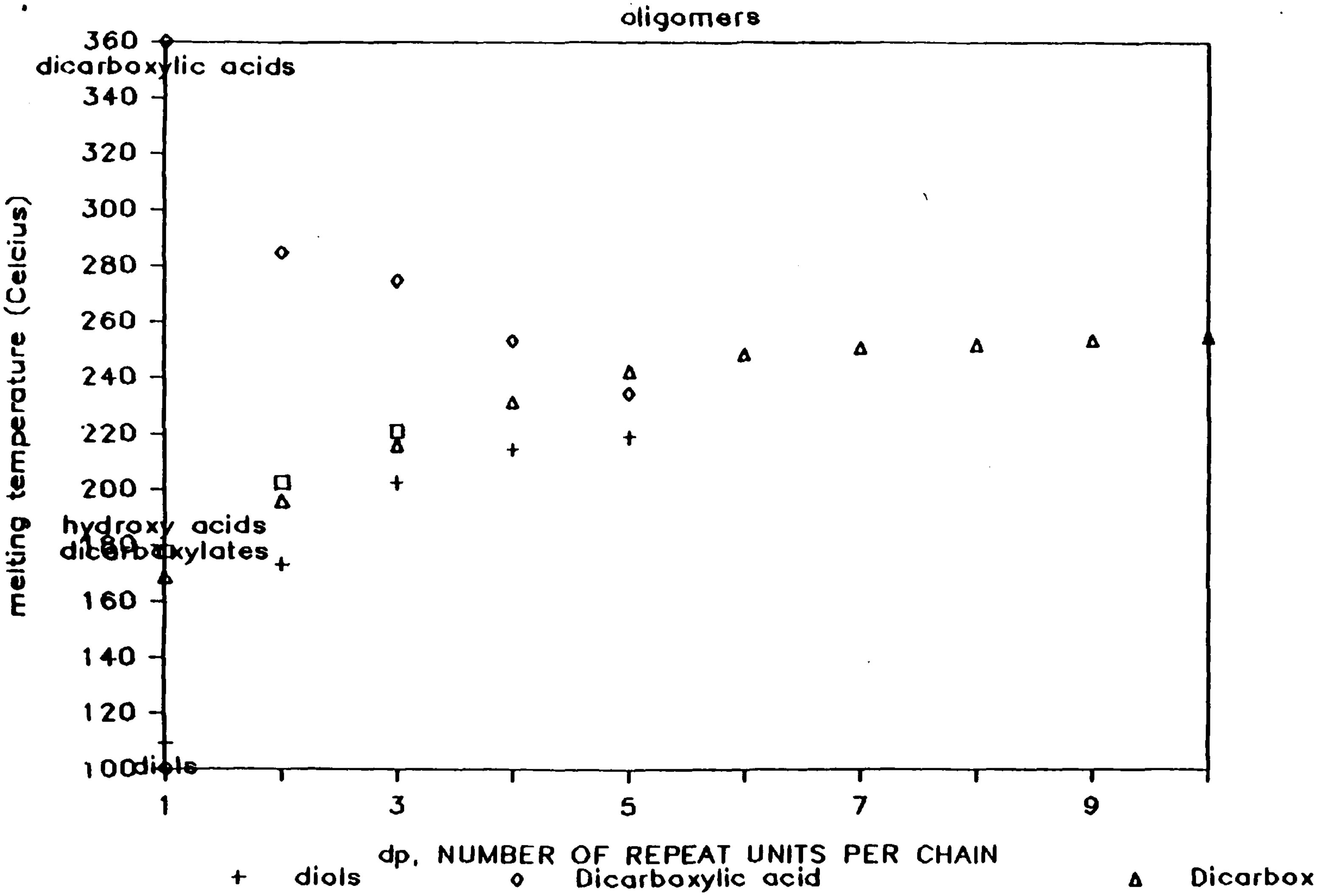


Figure 20:

PET: MOLECULAR WEIGHT *vs* Tg

K=0.0656, a=0.73

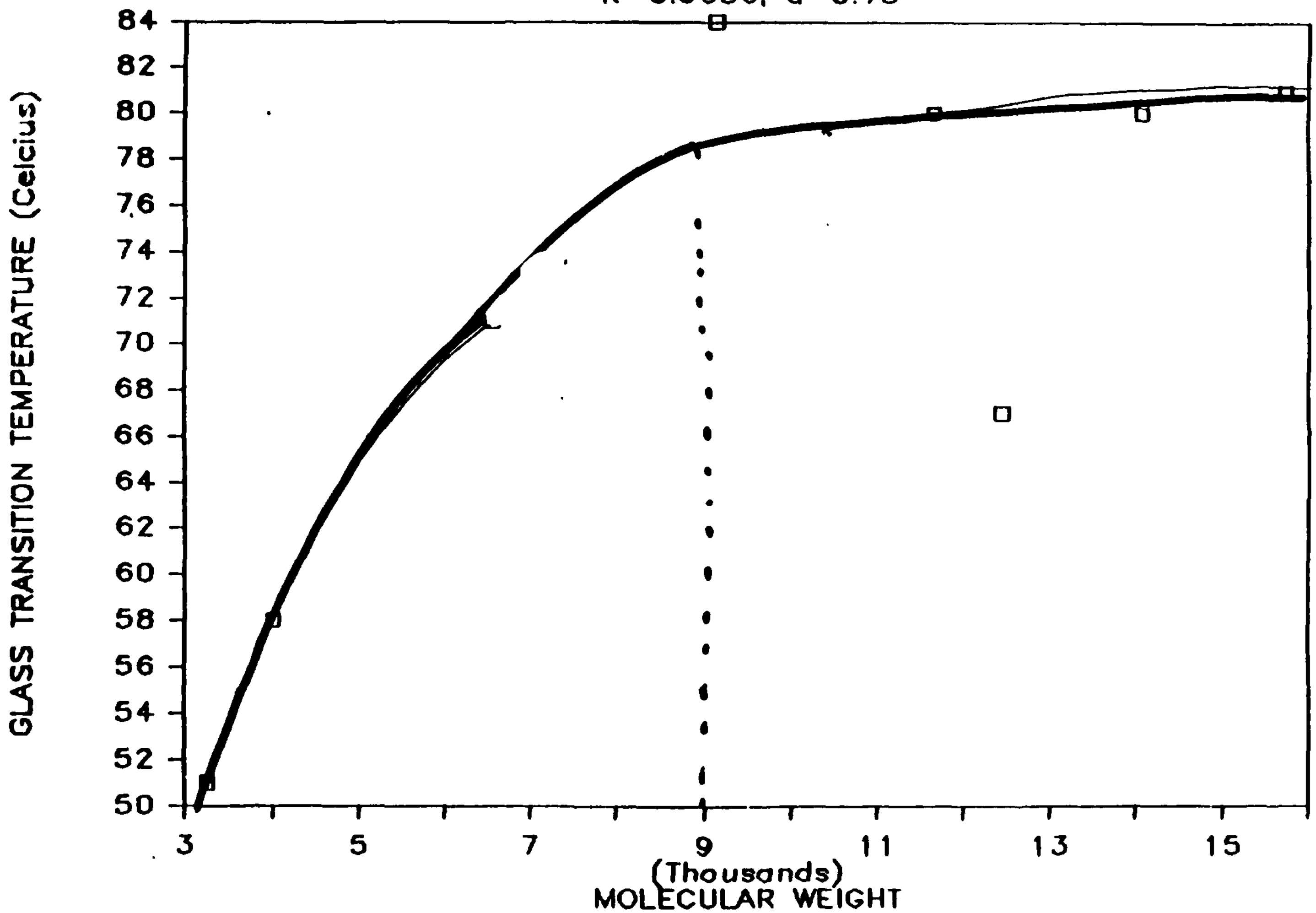
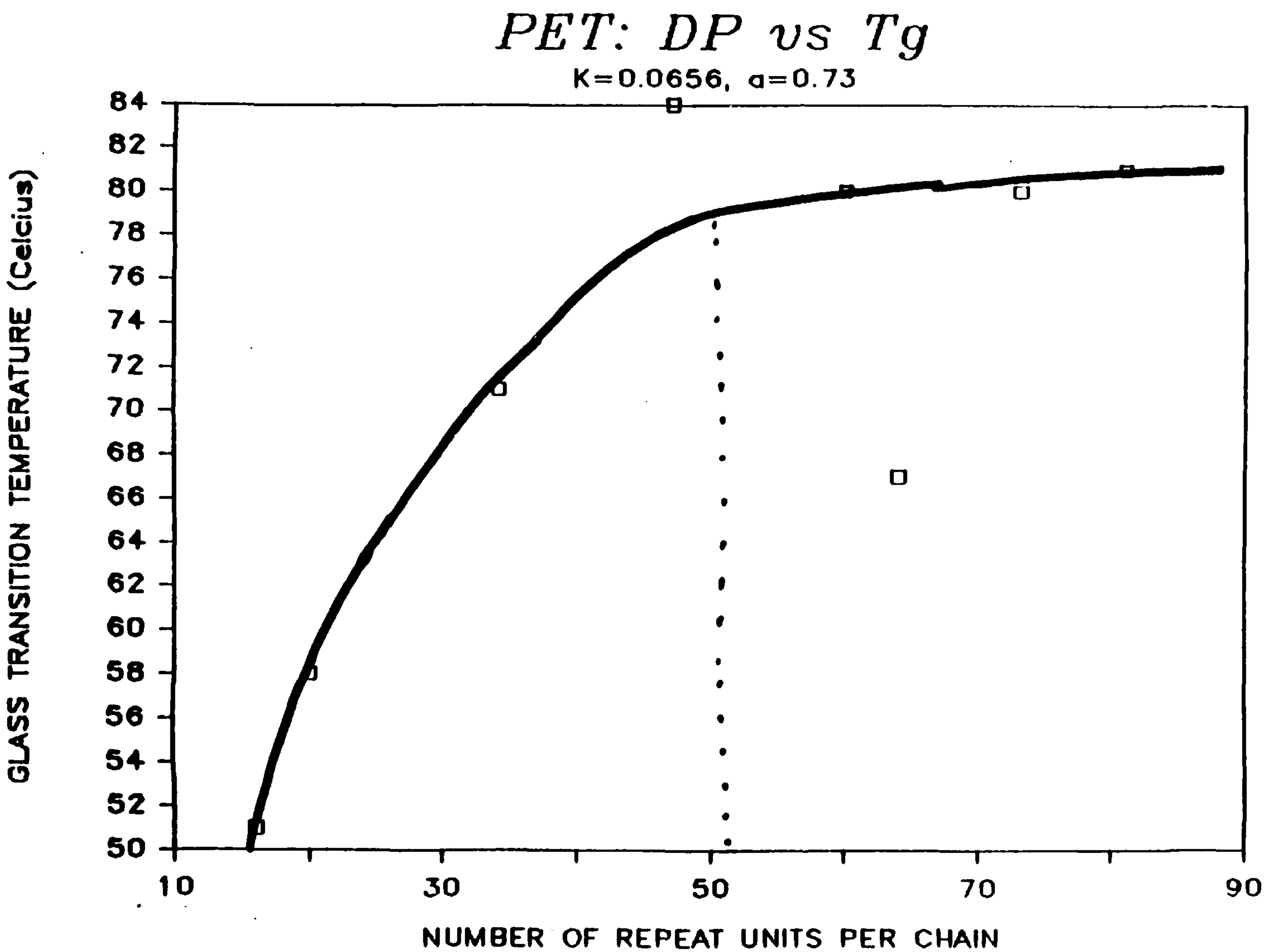


Figure 21



PET: DP vs Tg
K=0.0656, a=0.73
GLASS TRANSITION TEMPERATURE (Celcius)
84
82
80
78
76
74
72
70
68
66
64
62
60
58
56
54
52
50
10
30
50
70
90
NUMBER OF REPEAT UNITS PER CHAIN

Figure 22

PET: VISCOSITY vs Tg

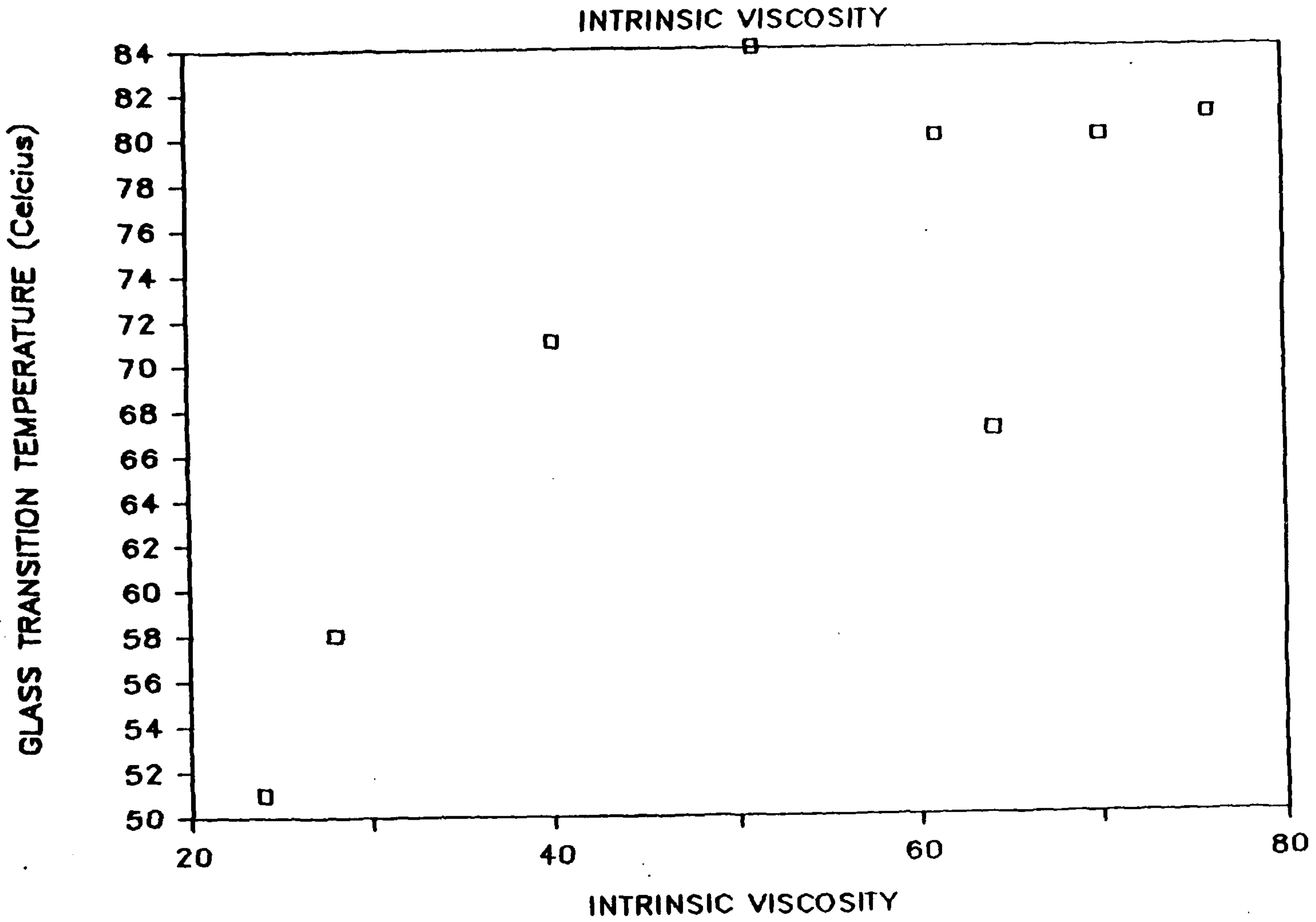


Figure 23:

REFERENCES

1. I.H. Zahn, G.B. Gleitsman, Agnew. Chem. Internat. Edit. 2, 410 (1963)
2. I.H. Zahn, H. Repin, Chem Ber. 103, 3041 (1970)
3. I.H. Zahn, R. Krzikalla, Makromol. Chem. 23, 31 (1957)
4. I.H. Zahn, C. Borstlap, G. Valk, Makromol. Chem. 64, 18 (1963)
5. I.H. Zahn, B. Seidel, Makromol. Chem. 29, 70 (1959)
6. R. Penisson, I.H. Zahn, Makrom. Chem. 133, 25 (1970)
7. H.J. Kolb, E.F. Izard, J. Appl. Phys. 20, 564 (1949)
8. J.March, "Advanced Organic Chemistry", Wiley, New York, pp. 345-346.
9. Patai, ed., "The Chemistry of the Ether Linkage", Wiley, New York, 1967.
10. Ref. 9, pp. 457-460, 468-470
11. D.D. Reynolds, W.O. Kenyon, J. Am. Chem. Soc. 72, 1593 (1950)
12. G.A. Olah, A.P. Fung, R. Malhotra, Synthesis, 474 (1981)
13. D.A.S. Ravens, I.M. Ward, Trans. Faraday Soc. 57, 150 (1961)
14. W.R. Moore, D. Sanderson, Polymer, 9, 153, (1968)
15. M.L. Wallach, Makromol. Chem., 103, 19 (1967)
16. J. Marshall, A.Todd, Trans. Faraday Soc., 49, 67 (1953)
17. I.M. Ward, Nature, 180, 141 (1957)

18. G. Meyerhoff, S. Shimotsuma, Makrom. Chem. 135, 195 (1970)

19. J.I.Scheinbeim et al., J. Appl. Phys. 50, 6101 (1979)

20. F.J. Lu, S.L. Hsu, Macromolecules 19, 326 (1986)

21. R.J. Shuford et al., Pol. Eng. and Sci. 16, (1976)

22. B.A. Newman et al., J. Appl. Phys. 50, 6095 (1979)

23. E.E. Havinga, P. van Pelt, Ber. Bunsenges. Phys. Chem. 83, 816 (1979)

24. C.C. Teng, A.F. Garito, Phys. Rev. Let. 50, 350, (1983)

25. S. Tamaru et al., J. Incl. Phen. 2, 885 (1984)

26. U.Y. Borovikov et al., Theor. Eksp. Khim. 10(2), 207, (1974)

27. B.V. Lapatin, Theor. Eksp. Khim. 13(4), 530, (1977)

28. A.A. Kane, I.F. Yupitzin, Zh. Obshch. Khim. 50(3), 1177, (1980)

29. O.B. Edgar, R. Hill, J. Polym Sci. 8, 1 (1951)

30. E.A. Collins, J. Bares, F.W. Billmeyer, jr., "Experiments in Polymer Science", Wiley, New York, 1973, p.147.

31. W.C. Still, M. Kahn, A. Mitra, J. Org. Chem. 43, 2923 (1978)

32. D.J. Williams, ed., "Non-Linear Optical Properties of Organic and Polymeric Materials," ASC Symp. Ser., 233 (1983)

33. Ref. 32, Ch. 1

34. R.W. Lenz, "Organic Chemistry of High Synthetic High Polymers", Wiley, New York 1967, Ch. 4.

35. S.J. Weininger, "Contemporary Organic Chemistry", Holt, New

York, 1972, Ch.18.

36. D.S. Kemp, F. Vellaccio, "Organic Chemistry", Worth, New York, 1980, p. 135.

37. J. Brandrup, E.H. Immergut ed., "Polymer Handbook", Wiley, New York.

38. Ref. 32, Ch. 3.

Appendix 3

TRANSMISSION OF ELECTRON DENSITY THROUGH MOIETIES BETWEEN DONORS AND ACCEPTORS: POSSIBLE IMPLICATIONS FOR NON-LINEAR OPTICS

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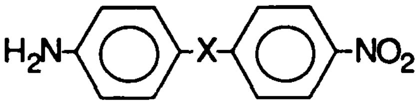
ABSTRACT

Organic materials having aminophenyl and nitrophenyl moieties linked by various atoms or groups (S, O, SO, SO_2, CH_2) were prepared and their ability to generate a second harmonic was compared within the series and with urea. We find that the compound containing a sulfur bridge, 4-amino-4'-nitrodiphenyl sulfide, exhibits a powder second harmonic generation efficiency which is approximately 10x that of urea. The result is consistent with earlier spectroscopic studies which indicate that sulfur, as opposed to the other bridges studied in this series, is effective in allowing the transmission of electron density between donors and acceptors.

INTRODUCTION

Organic molecules which are capable of partial intramolecular charge transfer and have noncentrosymmetric crystal structures are likely to exhibit second harmonic generation (SHG). Our interest in polymeric electro-optical materials has prompted us to examine the effectiveness of tetrahedral, flexible entities which connect the donor and acceptor in allowing 'communication' between the latter. The presence of such 'pivots' in the backbone or in pendant groups are expected to have a marked (and useful) influence on polymer properties (compare poly-p-phenylene and poly-p-phenylene sulfide), and it is important to understand their concomitant influence on electro-optical properties.

We have elected to study a series of molecules of general structure **1,** wherein a donor (aminophenyl) and an acceptor (nitrophenyl) are connected by various inorganic atoms or groups (**1a-e**).



1

	X =
1a	S
1b	O
1c	SO
1d	SO_2
1e	CH_2

This work was motivated by the results of ultraviolet [1] and NMR [2] spectroscopic studies on the series shown above which indicate that sulfur (**1a**) is very effective in allowing 'leakage' of electron density between the phenyl rings, possibly affording a reasonable value of the molecular quadratic hyperpolarizability, β. (Of course, for a reasonable SHG efficiency, the material must crystallize in a non-centrosymmetric structure, which is in fact the case for **1a** [3]; see below.) Szmant and McIntosh found that the UV spectrum of p-nitrophenyl phenyl sulfide

is identical to that of p-nitrophenyl methyl sulfide, suggesting that sulfur does not permit communication between these phenyls, although the spectrum of **1a** was found to have a λ_{max} which was red-shifted by about 3-5 nm. This led to the conclusion that sulfur will allow transmission of electron density when an 'incentive' is provided, i.e. when S is situated between a donor and an acceptor. The proton NMR study of Hyne and Greidanus reached a similar conclusion about the ability of sulfur to 'leak' electron density between phenyls in **1a**.

Of principal interest to us is the dependence of SHG intensity on the nature of X and, for selected cases, the dependence of efficiency on the number of repeat units separating donor and acceptor. The former is the subject of this report.

EXPERIMENTAL

The compounds of the series shown above were prepared following the procedures of Hyne and Greidanus [2]. Crystals of each were ground for several minutes with an agate mortar and pestle and pellets (1 cm diameter and ca. 0.1 mm thick) were then prepared by compressing the powders at 10 tons pressure. Second harmonic generation (SHG) efficiencies, normalized to that obtained from a pellet of urea, were determined at 532 nm using the 1064 nm fundamental output of a Q-switched Nd:YAG laser (Quanta-Ray DCR-2A). Just prior to impinging on the sample, the 1064 nm laser beam was passed through a Corning 7-54 colored glass filter to eliminate any collinear stray light in the 532 nm wavelength region. The 532 nm second harmonic was detected as light emerging from the powder samples in the forward direction. Two Schott KG-1 optical filters were used to block the forward propagating 1064 nm light and the 532 nm light was further filtered using a McPherson 0.2M monochromator. The optical SHG signal pulse was detected with a cooled RCA C31034 photomultiplier tube. After current amplification, each signal pulse from the photomultiplier was measured and digitized using a Stanford Research Systems gated integrator (Models 250 and 245) and then digitally stored. The SHG signal for a sample was taken as the average value obtained from 1000 laser pulses where the energy variation per laser pulse was less than 1%. For all the samples, both the temporal and spectral width of the optical signals were measured to insure that the detected signal was truly second harmonic light generated in the sample.

RESULTS AND DISCUSSION

Normalized SHG data from compounds **1a-e** are given in Table 1.

***Table 1.** SHG data (532 nm) for pellets of compounds **1a-e** normalized to a urea pellet*

X	SHG_{sample}/SHG_{urea}
S	9.8
O	2.3×10^{-3}
SO	2.1
SO_2	6.4×10^{-4}
CH_2	6.7×10^{-3}

The key result is that the compound **1a** is indeed capable of reasonable second harmonic generation. We are tempted to conclude that this observation is consonant with the spectroscopic data noted earlier which suggest that sulfur, with an appropriate 'incentive,' is capable of allowing transmission of electron density between phenyl rings. However, Abdel-Halim et al. [3] recently reported an independent SHG study of **1a** and, while they also show that this compound is SHG-active (20x better than urea), they suggest that there is no charge transfer interaction between the nitophenyl and the amino phenyl units. This conclusion was based on the facts that the bond at sulfur is nearly tetrahedral and the phenyls are orthogonal, and the reults of CNDO calculations which indicate that both the LUMO and HOMO show little contribution from the aminophenyl portion of the molecule. The X-ray crystal structure is particularly interesting in that it reveals the presence of close amino/nitro intermolecular contacts (suggestive of hydrogen bonding) which discourages the material from crystallizing centro- symmetrically. Thus, our anticipation that **1a** would be SHG-active based on the spectroscopic data may have been entirely fortuitous. However, we note that in poly(p-phenylene sulfide) the adjacent phenyls are nearly orthogonal and yet the band width is 1.2 eV, a relatively large value implying "that the sulfur atoms play an important role in connecting the conjugated systems of consecutive phenyl rings" [4]. This conclusion is supported by CNDO/S3 calculations [5] which also suggest that oxygens in poly(p-phenylene oxide) provide electronic 'connectivity' between adjacent phenyls. However, our data (Table 1) clearly show that the oxygen bridge (**1b**) is SHG-inactive. It may be that the more spatially extended 3p orbitals of sulfur are important in providing non-negligible overlap with the phenyl π-systems and could explain why the sulfoxide (**1c**) exhibits some SHG activity while the sulfone (**1d**) is inactive, although this argument becomes complicated by the fact that the sulfoxide and sulfone (particularly the latter) are electron-withdrawing moieties. As anticipated, the methylene bridge (**1e**) acts as an 'insulator' and is SHG-inactive.

We are studying several derivatives of of **1** in order to better understand the influence of the bridging atom or group on non-linear optical properties.

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REFERENCES

1. H. H. Szmant and J. J. McIntosh, *J. Am. Chem. Soc.*, **73**, 4356 (1951).

2. J. B. Hyne and J. W. Greidanus, *Can. J. Chem.*, **47**, 803 (1969).

3. H. Abdel-Halim, D. O. Cowan, D. W, Robinson, F. M. Wiygul and M. Kimura, *J. Phys. Chem.*, **90**, 5654 (1986).

4. J.-L. Brédas, in Handbook of Conducting Polymers, edited by T. Skotheim (Dekker, 1986) pp.893-894.

5. C. B. Duke and A. Paton, in Conductive Polymers, edited by R. B. Seymour (Plenum, 1981) pp. 162-165.